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Chemistry of Lime in Ammoniated Waters for SEALING CONCRETE PIPELINES

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Repairing cracks in concrete pipelines

used for irrigation water is expensive. The pipe must be excavated and patched from the outside or sealed on the inside if entry can be gained.

A less expensive method

involves the possibility of treating the flowing irrigation water with ammonia and other amendments so that lime will precipitate, adhere to the concrete, and seal the cracks.

This bulletin

is intended for irrigationists, agriculturists, engineers, concrete-pipe manufacturers, and any others concerned with large-scale irrigation operations and the repair of pipelines.

It reports results of laboratory studies on California waters and discusses the chemistry of lime formation and the nature of the precipitates.

In the Appendix you will find

- A technical discussion of the theory involved in precipitation and crystallization
- A discussion of the possibility of predicting lime precipitation qualitatively and quantitatively
- A table containing analyses of 83 representative California waters, against which a given water may be compared with respect to its possible capacity for precipitating lime

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In brief

here are some of the results of the experiments reported:

- Ammoniation of waters containing similar concentrations of Ca^{++} and HCO_3^-, but varying in Mg^{++} content, produced different levels of lime precipitation. Magnesium has an inhibiting effect on lime precipitation, depending on Ca^{++} content of the water.
- Coprecipitation of Mg^{++} with $CaCO_3$ occurred in measurable amounts in some waters, but this was not associated with Mg^{++} content, Mg:Ca ratio, or other parameters. When Mg^{++} precipitated in significant amounts, however, it was related to calculated $Mg(OH)_2$ precipitation. The precipitation of $Mg(OH)_2$ is a separate factor from the inhibiting effect of Mg.
- Common-ion Ca^{++} had a strong effect on lime precipitation in waters containing similar concentrations of HCO_3^- and Mg^{++} but varying in Ca^{++} content. Lime precipitation was greatly increased by addition of common-ion Ca^{++} to ammoniated waters containing adequate amounts of HCO_3^-. The inhibiting effect of Mg was partly overcome by adding Ca amendments.
- Waters deficient in Ca^{++} and HCO_3^- were reconstituted with Ca^{++} and HCO_3^- amendments to increase precipitation. Results show considerable promise for field application.
- Under magnification, a variety of crystalline forms was found in the precipitates, with calcite, vaterite, and aragonite predominant. All the crystals adhered strongly to glass flasks in the laboratory.
- For most waters, 100 ppm NH_3 are sufficient to promote precipitation.
- Application of amendments at the same point at which NH_3 is added is not recommended. Under field conditions, it will be necessary to introduce them separately, and with proper spacing, so that they are completely dissolved and mixed with the flowing water before it reaches the next injection site.

ABSTRACT

The sealing of leaky concrete pipelines involves the precipitation of crystalline lime ($CaCO_3$) from flowing ammoniated waters. Many waters are not suitable for lime precipitation, but can be corrected by the addition of amendments. This study reports on the forms of lime, rate of crystallization, buffer capacity, common-ion effects, coprecipitation, and inhibition. A laboratory method was developed to test waters for lime precipitation, to determine use of amendments, and to predict the quantity of precipitates and sealing action. The results have practical application to field conditions.

CHEMISTRY OF LIME IN AMMONIATED WATERS FOR SEALING CONCRETE PIPELINES[1,2]

INTRODUCTION

Sealing leaks in monolithic concrete pipelines commonly used for distribution of water is expensive. Leaks are generally repaired by excavating to the leak and either patching with a sealant or, if entry into the pipe is possible, sealing from the inside. A more economical method would be to treat flowing irrigation waters so that they would precipitate lime ($CaCO_3$) in pipelines.

The Chowchilla Water District in California sealed 159 out of 171 leaks in a three-mile length of 30- and 36-inch monolithic concrete pipelines by injecting anhydrous NH_3 into certain well waters flowing through the pipe (Eastman, 1966). Lime precipitating from these ammoniated waters adhered strongly to concrete surfaces, particularly within cracks and splits in the line. Preliminary tests conducted in the Chowchilla Water District, the Solano Irrigation District, and the Department of Water Science and Engineering at Davis indicated that many waters failed to precipitate lime selectively, and that their chemical composition and ammonia concentration are critical factors in such precipitation.

Well-documented measures are available for preventing lime precipitation and crustations in water lines of boilers and heaters, in flotation, in stabilization of sols, and in other industrial processes. The fertilizing of crops by injection of ammonia into water distributed through pipelines has been recognized as a hazardous procedure (Reitemeir and Buehrer, 1940) because lime crustations reduce flow and clog sprinkler jets.

Many unknown factors are involved in the formation of crystalline lime with adherence properties. The present study was conducted in an attempt to determine the conditions favorable for such precipitation. The first phase of the research involved a systematic examination of the effect of various dissolved salts, ammonia concentrations, and ambient conditions on lime precipitation. In order to separate the limiting

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variables, pure salt solutions were used in preference to natural waters. The second phase was concerned with the chemical characteristics of surface and ground water that are suitable for precipitation of lime. Waters with unsuitable chemical characteristics were reconstituted to the desired composition by addition of amendments, and then treated with ammonia.

An Appendix, beginning on page 33, discusses chemical equilibria and crystallization, and is intended to serve as a reference for interpretation and evaluation of the results obtained in this study.

LIME PRECIPITATION IN SALT SOLUTIONS

The first phase of the investigation was concerned with precipitation of lime in ammoniated salt solutions. Single and mixed salt solutions were examined to determine the effects of a particular solute or combination of solutes and NH_3 concentrations on lime formation. Prior to these studies, however, certain laboratory techniques and procedures were developed. The influence of temperature, buffer capacity, common ions, inhibiting effect of Mg, rate of crystallization, and crystalline species was investigated.

EXPERIMENTAL TECHNIQUES AND CONDITIONS

Analytical Methods

The study of precipitation from pure salt solutions was conducted under laboratory conditions and with glass containers. Initially, solutions prepared from chemically pure or reagent-grade salts were studied in preference to natural waters because the latter contain dissolved materials varying in composition and concentration. By using known salt solutions, we could control the number of variables and study their effects comprehensively.

Laboratory glassware allowed direct microscopic observations of the precipitants. From the standpoints of adhesion and presence of colloidal impurities which may act as seeds for crystallization, the relatively rough surface of concrete pipe should be more conducive to precipitation than was the smooth glassware surface.

Standard analytical methods (Richards, 1954; Orland, 1965) were employed. Calcium and magnesium were determined by EDTA (ethylenediamine tetraacetate) titration or by flame photometry. The flame photometric method was also used for sodium. The carbonates and hydroxide were titrated with standard acid, and pH was measured with an expanded-scale pH meter. Sulfate was determined turbidimetrically; chloride, by titration with silver nitrate.

The amount of calcium precipitated from solutions was determined by differences between initial and final Ca^{++} values. In general the calcium precipitated in ammoniated waters is in the $CaCO_3$ form, and only trace amounts may precipitate as other Ca salts in natural waters. The final analysis for Ca^{++} was made on supernatant solu-

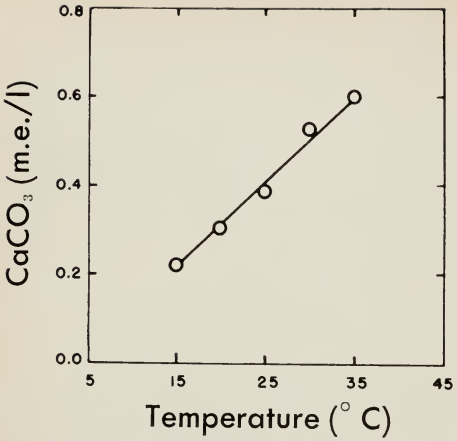


Fig. 1. Effect of temperature on the precipitation of lime in 1.56 m.e. per liter $Ca(HCO_3)_2$ solution treated with 100 ppm NH_3.

tions obtained by filtering the ammoniated solution through No. 41 Whatman filter paper. Stock solutions of aqueous $NH_3(NH_4OH)$ were approximately 1 N in strength, to initiate crystallization and to simulate the injections of anhydrous NH_3 in water. Stock $Ca(HCO_3)_2$ salt solutions, $\pm$ 5 m.e. per liter, were prepared by dissolving $CaCO_3$ under 0.2 atmosphere of CO_2.

Effect of Temperature

Laboratory room temperatures were about 22 $\pm$ 2°C. The temperature effect on lime precipitation in an ammoniated $Ca(HCO_3)_2$ salt solution over a six-hour period is shown in figure 1. Increases in temperature lower the solubility of NH_3 and CO_2 in water. Conversely, increases in temperature cause a greater dissociation of aqueous NH_3 into OH^- and NH_4^+ and a greater ionization of HCO_3^- into $CO_3^=$ and H^+. The net result of rising temperature was an increase in precipitation.

Buffer Capacity and Spontaneous Precipitation

A series of $Ca(HCO_3)_2$ salt solutions, ranging in concentration from 0.5 to 5.3 m.e. per liter, were titrated with NH_3 solution in a closed system, with continuous stirring. The pH titration curves for these buffered HCO_3^- solutions are presented in figure 2. Small additions of NH_3 to the 0.5 and 1.3 m.e. per liter salt solutions caused rapid changes in pH up to an NH_3 concentration of about 100 ppm. Thereafter, further titration with this weak base resulted in only small changes in pH. As the HCO_3^- concentration increases, its buffer capacity increases, and more NH_3 is required to obtain a unit pH change than is required in less concentrated solutions. Spontaneous precipitation was detected when the pH of the solutions was raised to 9 or slightly higher. The ammoniated solutions at this pH range are at a state of supersaturation (Appendix fig. 1) with respect to $CaCO_3$. Nucleation and crystal growth can probably occur at lower pH, but not spontaneously.

Rate of Crystallization

Ammonia was applied at rates of 50, 75, 100, 150, and 200 ppm to a salt solution containing 1.56 m.e. per liter of $Ca(HCO_3)_2$. Following the addition of NH_3, the solutions were shaken and allowed to stand for 2, 8, 24, 48, and 96 hours of precipitation time. The ammoniated solutions were then analyzed for Ca^{++} and pH. Spontaneous precipitation did not occur and crystal formation was relatively slow. Microscope observations (100 $\times$ magnification) of the two-hour series indicated the presence of particles ranging in distribution from sparse (50 ppm NH_3) to numerous (200 ppm NH_3), which could not be positively identified. Apparently these minute particles were nuclei or crystal seeds. Similar particles were found with

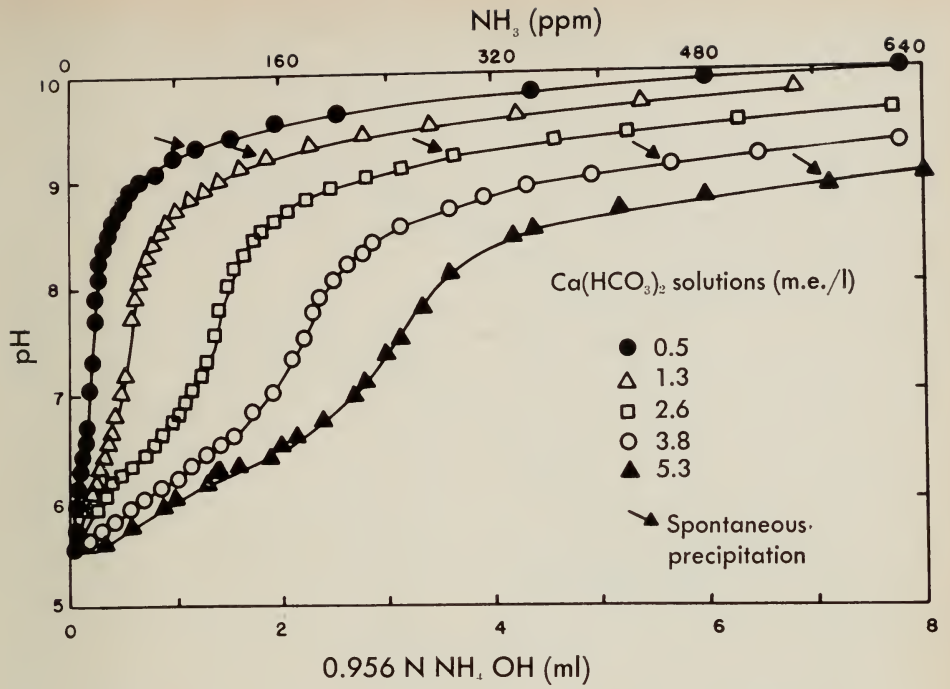


Fig. 2. Buffer capacity of $Ca(HCO_3)_2$ salt solutions, and the NH_3 concentration and pH at which spontaneous precipitation takes place.

the eight-hour series, except that the solution treated with 200 ppm NH_3 contained identifiable calcite and aragonite crystals (Appendix fig. 3). With increasing precipitation time, the size of the crystals was larger for a given level of NH_3. With increasing NH_3 concentrations, the number of crystals increased for a given time period. Lime precipitated in the bottom and adhered strongly to the flasks.

The amount of $CaCO_3$ precipitated for a given NH_3 concentration at different quiescent time periods is given in figure 3. Lime precipitation was increased either by lengthening precipitation time or by increasing NH_3 concentration. The pH of the solutions is shown in figure 4. The 48-hour pH values fell between the 24- and 96-hour series. Because of insufficient $CO_3^=$ very little $CaCO_3$ was formed below pH 8.5.

Cyclic Precipitation and Renewal

In the field, a more dynamic condition exists than that in the laboratory. Anhydrous NH_3 is introduced into water as it flows past the point of injection. Because of differences in velocity distribution, the water is continuously mixed or agitated in the pipeline. Deposition of nuclei and crystals on previous deposition sites or on new areas occurs as ammoniated water flows past each cross-section. For example, if a ½-mile section of the distribution line is to be treated with NH_3, the amount of water required to fill that pipeline is in proportion to its diameter. The time required to fill or displace the water in the line at a flow rate of 1 cfs (cubic

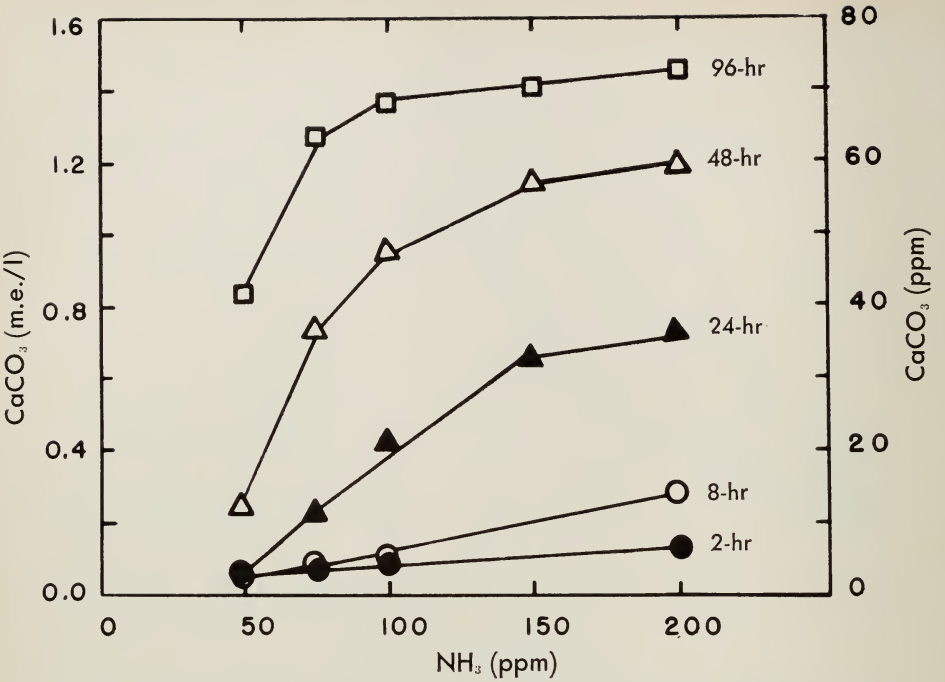


Fig. 3. Relations between $CaCO_3$ precipitation and NH_3 concentrations for different quiescent precipitation periods. The initial concentration of $Ca(HCO_3)_2$ was 1.56 m.e. per liter.

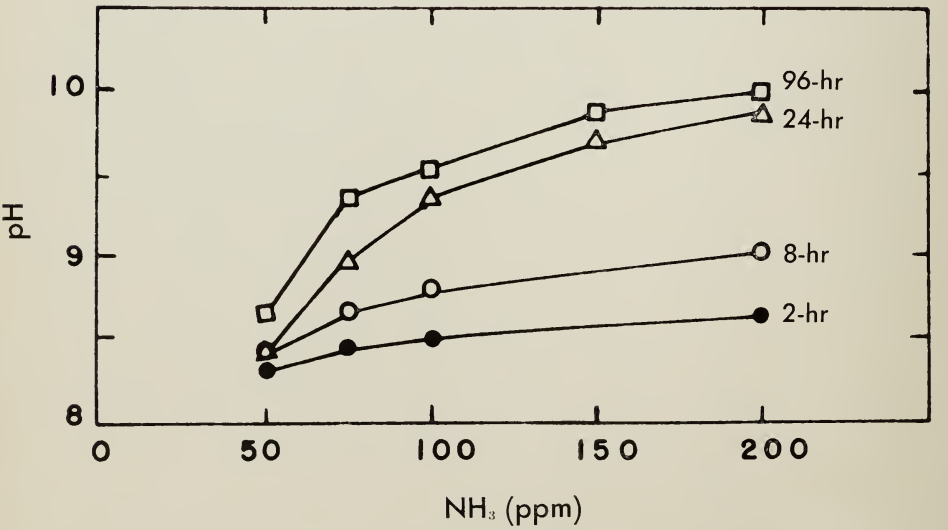


Fig. 4. The pH of ammoniated $Ca(HCO_3)_2$ solutions for different quiescent precipitation times. Initial pH was 6.80.

feet per second) is as follows:

PIPE DIAMETER *inches*	CAPACITY WHEN FULL *cu. ft.*	TIME TO FILL AT 1 CFS *hrs.*
24	8,290	2.30
30	12,931	3.59
36	18,652	5.18
42	25,366	7.05
48	33,158	9.20

The ammoniated water may be successively displaced and released downstream until leaks are sealed to the operator's satisfaction. To duplicate such a condition in the laboratory would require a model, and then only limited measurements and observations could be obtained without elaborate instrumentation. Instead, the following laboratory technique was used. In successive six-hour periods, lime was precipitated from ammoniated salt solutions in a flask. At the end of each period, the solution was replaced with a fresh one. In addition, the reaction flasks were placed on a horizontal shaking machine set at 60 oscillations (1-inch strokes) per minute to simulate movement of water in pipelines. This experiment was continued through eight cycles of six-hour precipitations with NH_3 rates of 25, 50, 75, 100, and 200 ppm. Results are presented in figures 5 and 6.

For a given NH_3 concentration (fig. 5) lime precipitation increased with number of cycles, except for the 25-ppm NH_3 treatment. The deposit of nuclei and crystals from the previous cycles tended to intensify crystallization from succeeding solutions. The critical NH_3 concentration was about 75-ppm NH_3. The range of pH obtained from these treatments is shown in figure 6, for three selected cycles. The amount of lime precipitated and the pH for the eighth cycle of this study are

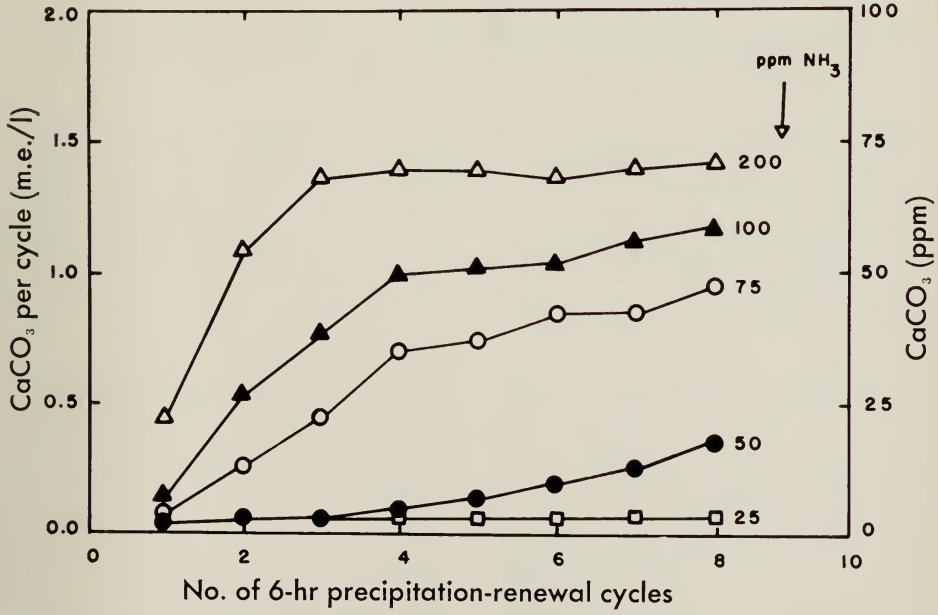


Fig. 5. Relations between $CaCO_3$ precipitation and NH_3 concentration for successive cycles of 6-hour precipitation and renewal of ammoniated $Ca(HCO_3)_2$ solutions. Initial $Ca(HCO_3)_2$ concentration was 1.58 m.e. per liter.

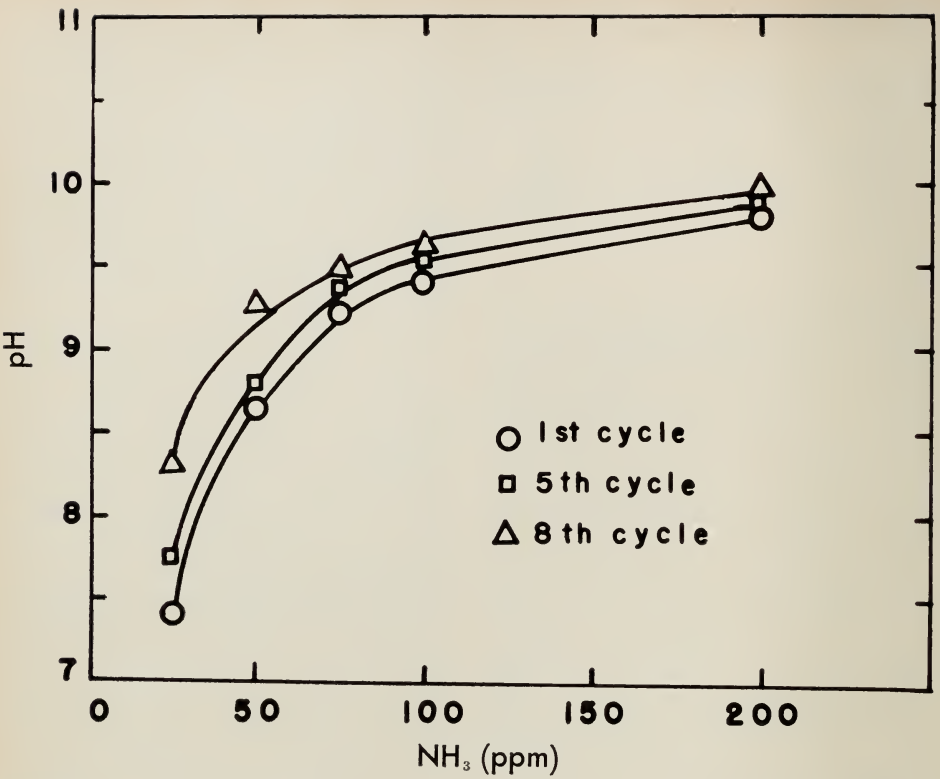


Fig. 6. The pH of $Ca(HCO_3)_2$ solutions ammoniated to varying degrees and undergoing cyclic 6-hour precipitation and renewal. Initial pH of the $Ca(HCO_3)_2$ solution was 6.89.

similar to those for the 48-hour quiescent treatment in the study on crystallization rate.

Minute specks of barely discernible calcite were observed in the 25-ppm NH_3 flasks after eight cycles of precipitation. Large calcite crystals with fewer smaller ones were found in the bottom of the 50-ppm NH_3 flasks. A profuse growth of calcite and aragonite, with many smaller, single crystals, was observed in the 75-ppm NH_3 flasks, with some $CaCO_3$ adhering to the walls of the vessel. With the 100-ppm NH_3 treatment, a heavy deposit of calcite and aragonite crystals covered the entire flask up to the water level. By the eighth cycle, precipitation in 200-ppm NH_3 solutions was so dense that individual crystals were not discernible. The flask was opaque, and glazed over to such a degree that very little light was transmitted for microscopic observations.

Procedure Adopted

A rapid technique for determining data related to field conditions is desirable for facilitating large-scale studies on the effect of dissolved salts on lime precipitation. The cyclic precipitation and renewal experiment approached field conditions; however, it is a time-consuming method and permits only a few salt solutions to be systematically examined within a reasonable time. In

view of the close approximation of data obtained from the 48-hour precipitation (fig. 3) with that of eight cycles of precipitation and renewal (fig. 5), the former procedure was selected.

The initial pH and concentration of the HCO_3^- ion influence the amount of NH_3 required for lime formation (fig. 2). A solution containing about 1.58 m.e. per liter of $Ca(HCO_3)_2$ was chosen as the base solution for the addition of various salts. The concentration of salt admixture to the $Ca(HCO_3)_2$ solution was in ratios of 0.5, 1, 2, and 4. The pH of the solution mixtures was then adjusted to about 6.85, before ammoniation, by adding minute amounts of a strong base (NaOH) or acid (HCl).

A 100-ml subsample of the salt solution was measured into 125-ml Erlenmeyer flasks, aqueous NH_3 (NH_4OH) from a 0.934 N stock solution was added, the solution was mixed, stoppered, and allowed to stand under room conditions. Concentrations of ammonia were 50, 75, 100, 150, and 200 ppm. After 48 hours, the ammoniated solution was filtered, and Ca^{++} and pH of the filtrate were measured. The amount of lime precipitated was the difference between the initial and final Ca^{++} content. The precipitants were examined by microscope at 100 × magnification, for the presence of $CaCO_3$ and other crystalline or amorphous particles. All treatments were replicated threefold.

SALT-SOLUTION STUDIES

Influence of Neutral Salts on Precipitation

The influence of seven different salts on lime precipitation from ammoniated $Ca(HCO_3)_2$ solutions was investigated. The neutral salts studied were NaCl, Na_2SO_4, and $MgCl_2$, representing 1–1, 1–2, and 2–1 electrolytes, respectively. The amounts of lime precipitating for different levels of added NH_3 are shown in table 1. For a given ratio of salt added to $Ca(HCO_3)_2$, symmetry concentration (SC), higher NH_3 rates increased the amount of lime formed. Varying the concentration of neutral Na salt (NaCl, Na_2SO_4) produced little or no effect on lime precipitation for comparable NH_3 additions. However, admixtures of $MgCl_2$ resulted in smaller amounts of lime precipitation (fig. 7), and with increasing symmetry concentration this effect became more pronounced.

The ionic activity coefficient for divalent ions (Ca^{++} and $CO_3^=$ before precipitation) in solutions containing 200 ppm NH_3 and at symmetry concentration 4 was calculated to be 0.94 for the NaCl and 0.93 for the Na_2SO_4 and $MgCl_2$ systems. Since the Cl^- in the NaCl system had no significant effect on lime precipitation, Mg^{++} of the $MgCl_2$ system must be the ion that interferes with or inhibits lime formation.

Influence of Common Ion HCO_3^- on Precipitation

The admixture of the common ion HCO_3^-, more correctly the $CO_3^=$ formed upon ammoniation (equation [11], Appendix A), resulted in greater lime precipitation than did the neutral salt admixtures (table 2). The common-ion effect may be described by referring to equation [9] (Appendix A). When $CO_3^=$

TABLE 1

EFFECT OF NEUTRAL SALTS AND VARIOUS CONCENTRATIONS OF NH_3 ON LIME PRECIPITATION AFTER 48 HOURS

Symmetry concentration*	NH_3 added	Added salt					
		NaCl		Na_2SO_4		$MgCl_2$	
		$CaCO_3$	pH	$CaCO_3$	pH	$CaCO_3$	pH
	ppm	*m.e./l*		*m.e./l*		*m.e./l*	
0.5	0	1.56†	6.84†	1.56†	6.85†	1.58†	6.84†
	50	1.02	9.49	0.98	9.56	0.70	9.47
	75	1.17	9.70	1.15	9.72	1.04	9.64
	100	1.28	9.85	1.24	9.92	1.14	9.78
	150	1.35	10.00	1.33	10.03	1.24	9.96
	200	1.40	10.09	1.36	10.12	1.24	10.08
1.0	0	1.56†	6.85†	1.56†	6.86†	1.58†	6.85†
	50	0.94	9.53	0.98	9.68	0.59	9.40
	75	1.22	9.71	1.23	9.79	0.98	9.64
	100	1.23	9.84	1.25	9.85	1.12	9.82
	150	1.31	10.02	1.33	10.02	1.20	9.98
	200	1.32	10.12	1.37	10.16	1.21	10.10
2.0	0	1.56†	6.86†	1.56†	6.86†	1.58†	6.87†
	50	1.00	9.58	1.00	9.39	0.48	9.44
	75	1.13	9.78	1.12	9.62	0.87	9.58
	100	1.25	9.95	1.25	9.83	1.02	9.69
	150	1.29	10.07	1.32	10.00	1.09	9.88
	200	1.36	10.10	1.35	10.13	1.16	9.98
4.0	0	1.56†	6.87†	1.56†	6.85†	1.58†	6.88†
	50	0.98	9.63	0.83	9.60	0.27	9.42
	75	1.04	9.77	0.94	9.77	0.64	9.59
	100	1.16	9.89	1.13	9.87	0.86	9.72
	150	1.25	10.04	1.26	10.03	1.04	9.87
	200	1.30	10.13	1.29	10.17	1.10	10.01

* Concentration ratio of added salt to $Ca(HCO_3)_2$.
† Initial concentration and pH of $Ca(HCO_3)_2$ solution.

(or Ca^{++}) is added to a saturated lime solution, the concentration (activity) of Ca^{++} (or $CO_3^{=}$) is depressed since K_{CaCO_3} is a fixed value. The decrease in Ca^{++} (or $CO_3^{=}$) concentration leads to a lower solubility of lime and hence greater precipitation. With increasing additions of common ion (either $CO_3^{=}$ or Ca^{++}) to this solution, further decreases in solubility would occur.

In the $NaHCO_3$ series, increases in the concentration of added HCO_3^- produced no significant effect on lime precipitation for given rates of NH_3. Contrary to the lime solution cited above, the salt solution mixture of $Ca(HCO_3)_2$ and $NaHCO_3$ was not initially a saturated solution of lime. In order for lime to precipitate, NH_3 was added to convert HCO_3^- to $CO_3^{=}$. The $CO_3^{=}$ formed then reacted with Ca^{++} to form lime. By increasing the concentration ratio of $NaHCO_3$ to $Ca(HCO_3)_2$ the buffer capacity of the solution was also increased, which fortuitously counteracted the common-ion effects in this system. The relationship between HCO_3^- concentration and buffer capacity of salt solutions is illustrated in figure 2, where additional NH_3 was required to attain a given pH level as the HCO_3^- concentration increased. The pH values

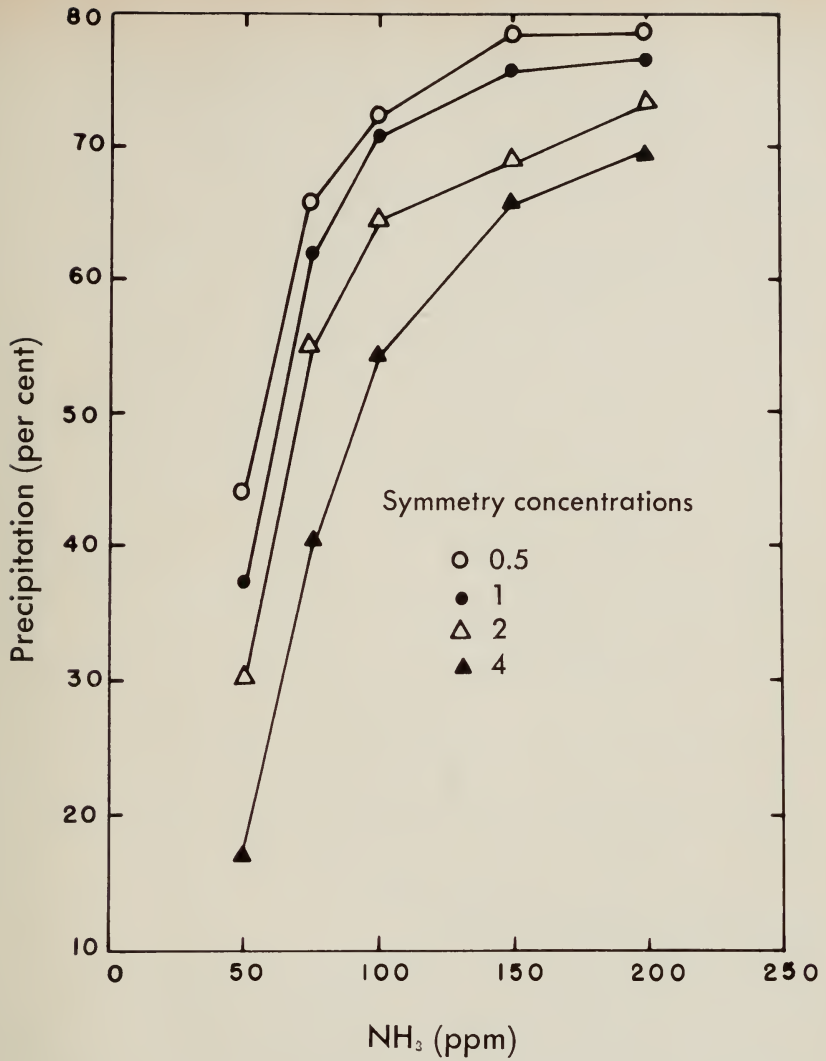


Fig. 7. Average percentage precipitation of Ca^{++} as $CaCO_3$ for several NH_3 concentrations in $MgCl_2$ admixtures of varying symmetry concentrations (SC).

for the $NaHCO_3$ system (table 2), as compared with the NaCl system (table 1), were found to be lower, substantiating the buffer action of added HCO^-_3. Further increases in $NaHCO_3$ would probably result in a decrease in lime precipitation and pH as the buffer action overcame the common-ion effect. Although the common-ion effect was subdued to a certain extent in the $NaHCO_3$ series, precipitation of lime was greater when compared with the NaCl and Na_2SO_4 systems (fig. 8).

In contrast, lime precipitation was reduced as the concentration ratio of $Mg(HCO_3)_2$ was raised (table 2). The buffer capacity of $Ca(HCO_3)_2$ solutions was increased with additions of HCO^-_3 as was the case for the $NaHCO_3$ system. With the exception of the 0.5 ratio

TABLE 2

EFFECT OF THE COMMON ION HCO_3^- AND VARIOUS CONCENTRATIONS OF NH_3 ON LIME PRECIPITATION AFTER 48 HOURS

Symmetry concentration*	NH_3 added	Added salt			
		$NaHCO_3$		$Mg(HCO_3)_2$	
		$CaCO_3$	pH	$CaCO_3$	pH
	ppm	*m.e./l*		*m.e./l*	
0.5	0	1.57†	6.86†	1.59†	6.84†
	50	1.15	9.38	0.98	9.39
	75	1.26	9.57	1.13	9.68
	100	1.39	9.73	1.20	9.83
	150	1.42	9.87	1.27	10.01
	200	1.43	10.01	1.30	10.10
1.0	0	1.57†	6.86†	1.59†	6.85†
	50	1.02	9.32	0.99	9.20
	75	1.19	9.51	1.07	9.49
	100	1.32	9.67	1.17	9.67
	150	1.39	9.86	1.28	9.86
	200	1.41	9.98	1.29	10.00
2.0	0	1.57†	6.86†	1.59†	6.84†
	50	0.92	9.20	0.88	9.02
	75	1.25	9.46	1.02	9.25
	100	1.36	9.66	1.14	9.44
	150	1.42	9.83	1.18	9.67
	200	1.43	9.94	1.29	9.85
4.0	0	1.57†	6.86†	1.59†	6.86†
	50	0.95	9.12	0.74	8.67
	75	1.30	9.39	0.91	8.92
	100	1.39	9.52	1.02	9.13
	150	1.42	9.76	1.14	9.38
	200	1.43	9.86	1.19	9.60

* Concentration ratio of added salt to $Ca(HCO_3)_2$.
† Initial concentration and pH of $Ca(HCO_3)_2$ solution.

solutions, pH values were lower in $Mg(HCO_3)_2$ than in $MgCl_2$ systems for identical rates of NH_3. In addition to the buffer effect, Mg apparently inhibited lime formation, as was the case with the $MgCl_2$ system. The combined effects of buffer action and inhibition by Mg are shown in figure 9. With the lowest concentration of $Mg(HCO_3)_2$, percentage of precipitation was less than with $NaHCO_3$, and with increasing $Mg(HCO_3)_2$ concentrations precipitation was reduced. Apparently the beneficial effects of common ion were nearly nullified by the buffer action and Mg interference, as shown by the curves for $MgCl_2$ and $Mg(HCO_3)_2$.

The exact mechanism(s) by which Mg inhibited lime formation is not known. The degree of coprecipitation of Mg^{++} with $CaCO_3$ was relatively insignificant (0.1 m.e. or less per liter), with Mg^{++} concentrations in the $Ca(HCO_3)_2$ solutions ranging from about 0.8 to 6.4 m.e. per liter. In a previous study (Doneen, 1964), Mg^{++} coprecipitated in significant amounts in $Ca(HCO_3)_2$ solutions only when the Mg^{++} concentrations exceeded 20 m.e. per liter. Several views on the inhibiting mechanisms of Mg are found in the literature (Brooks, Clark, and Thurs-

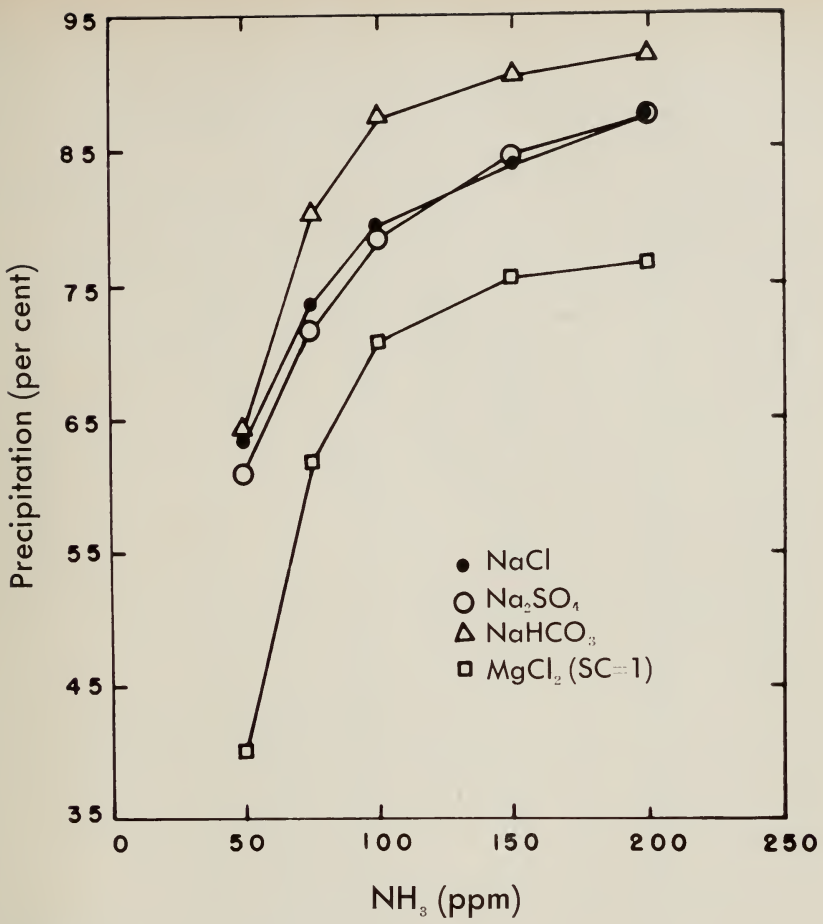


Fig. 8. Average percentage of precipitation of Ca^{++} as $CaCO_3$ for different NH_3 rates in Na-salt admixtures and in $MgCl_2$ with a symmetry concentration (SC) of 1.

ton, 1950; Akin and Lagerwerff, 1965*b*; Berner, 1966).

Influence of Common Ion Ca^{++} on Precipitation

The addition of common ion Ca^{++}, as $CaCl_2$ and $CaSO_4$, to HCO_3^- solutions promoted precipitation of $CaCO_3$ (table 3). Lime precipitation was increased by increasing NH_3 concentration for a given symmetry concentration and by increasing symmetry concentration for a given level of ammoniation. For the pH range of 6.85 to 6.88, about 80 per cent or less of the total dissolved CO_2 existed as HCO_3^- and the remainder as aqueous CO_2 and H_2CO_3 (Appendix fig. 1). In the presence of Ca salt admixtures, nearly all of the dissolved CO_2 was involved in $CO_3^=$ formation, leading to precipitation values in excess of the initial 1.58 m.e. per liter of HCO_3^-. Under closed-system conditions (Appendix A equation [18]), each equivalent of HCO_3^- forms two of $CaCO_3$. The percentage precipitations of total Ca^{++} for symmetry concentration solutions of 0.5 and 1 were similar, and the aver-

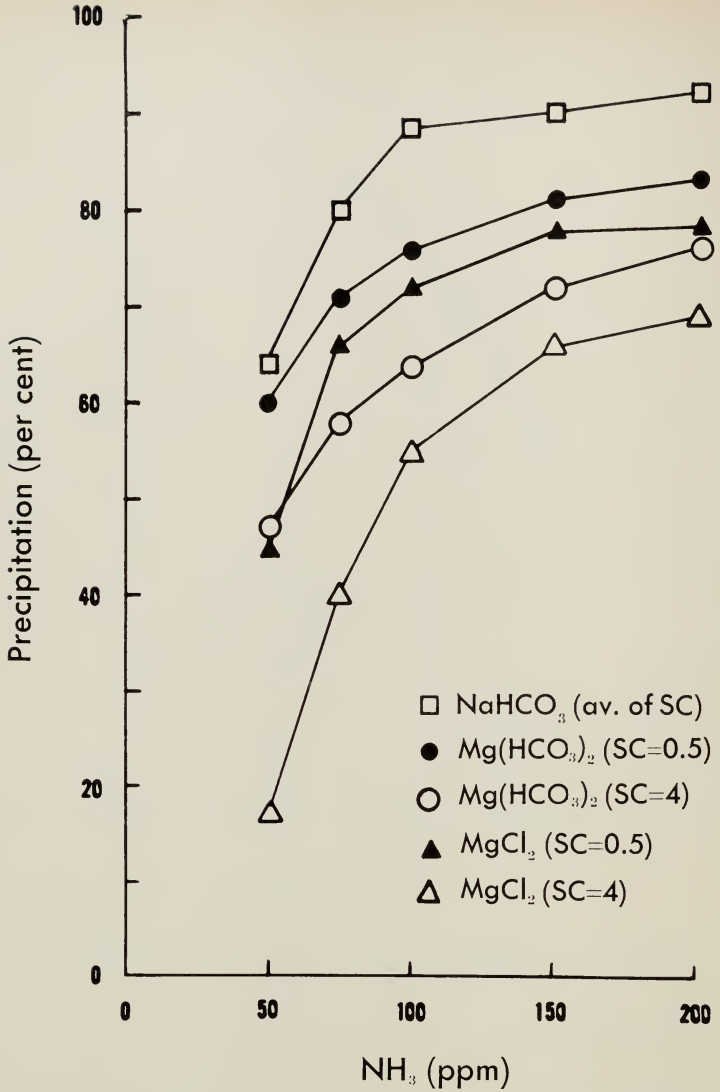


Fig. 9. Average percentage precipitation of Ca^{++} as $CaCO_3$ in $Ca(HCO_3)_2$ solutions ammoniated to several levels and containing $Mg(HCO_3)_2$, $MgCl_2$, and $NaHCO_3$ of varying symmetry concentrations (SC).

age values are plotted in figure 10. As the symmetry concentration of the Ca salt admixture increased, the percentage precipitation decreased because HCO_3^- (also aqueous CO_2) was the limiting constituent. The Ca^{++} precipitated from $CaCl_2$ and $CaSO_4$ systems is of the same order of magnitude for each symmetry concentration. The average percentage precipitation of Ca^{++} in the common-ion $NaHCO_3 + Ca(HCO_3)_2$ mixtures is comparable with the average values of common-ion $CaCl_2 + Ca(HCO_3)_2$ and $CaSO_4 + Ca(HCO_3)_2$ mixtures, with symmetry concentrations of 0.5 and 1 (fig. 10).

TABLE 3

EFFECT OF THE COMMON ION Ca^{++} AND VARIOUS CONCENTRATIONS OF NH_3 ON LIME PRECIPITATION AFTER 48 HOURS

Symmetry concentration*	NH_3 added	Added salt			
		$CaCl_2$		$CaSO_4$	
		$CaCO_3$	pH	$CaCO_3$	pH
	ppm	*m.e./l*		*m.e./l*	
0.5	0	2.34†	6.86†	2.30†	6.85†
	50	1.52	9.30	1.49	9.31
	75	1.93	9.60	1.85	9.63
	100	2.08	9.74	1.97	9.74
	150	2.18	9.91	2.10	9.92
	200	2.18	10.03	2.15	10.04
1.0	0	3.14†	6.88†	3.11†	6.86†
	50	2.21	9.11	2.07	9.22
	75	2.73	9.42	2.61	9.47
	100	2.86	9.62	2.78	9.68
	150	2.92	9.83	2.90	9.92
	200	2.96	9.97	2.95	10.05
2.0	0	4.61†	6.85†	4.54†	6.85†
	50	2.57	9.07	2.40	9.15
	75	3.24	9.15	3.16	9.42
	100	3.37	9.40	3.34	9.63
	150	3.55	9.83	3.50	9.84
	200	3.65	9.94	3.62	10.00
4.0	0	7.31†	6.80†	7.63†	6.86†
	50	3.02	8.43	3.56	8.69
	75	4.12	9.02	4.43	9.19
	100	4.28	9.32	4.70	9.42
	150	4.44	9.65	4.81	9.72
	200	4.51	9.83	4.86	9.94

* Concentration ratio of added salt to $Ca(HCO_3)_2$.
† Initial pH and total Ca^{++} of salt solution mixture.

Another study on lime chemistry (Akin and Lagerwerff, 1965*b*) reported that Mg^{++} and $SO_4^{=}$ enhanced the solubility of calcium carbonate. Our study showed no significant difference between a Cl^- and $SO_4^{=}$ system in the absence of Mg^{++}. The formation of metastable $CaCO_3$ with a higher solubility than calcite is a distinct possibility in the presence of Mg^{++} and could be interpreted as an inhibition effect. On the other hand, undissociated forms of $CaSO_4$ and $MgSO_4$ (Tanji and Doneen, 1966*b*) and other complexes which may exist in solutions containing Mg^{++}, Ca^{++}, and $SO_4^{=}$ may cause less lime to precipitate.

Nature of Crystals

In treatments that produced a small precipitation from the ammoniated salt solutions, the deposits were exclusively on the bottoms of the flasks. With a greater precipitation, crystals were deposited and grew in more or less uniform density up to the water level in the containers. The precipitates adhered to the glass and were not dislodged by vigorous shaking nor by a stream of water from the faucet.

Generally speaking, the number of crystals increased and the size decreased

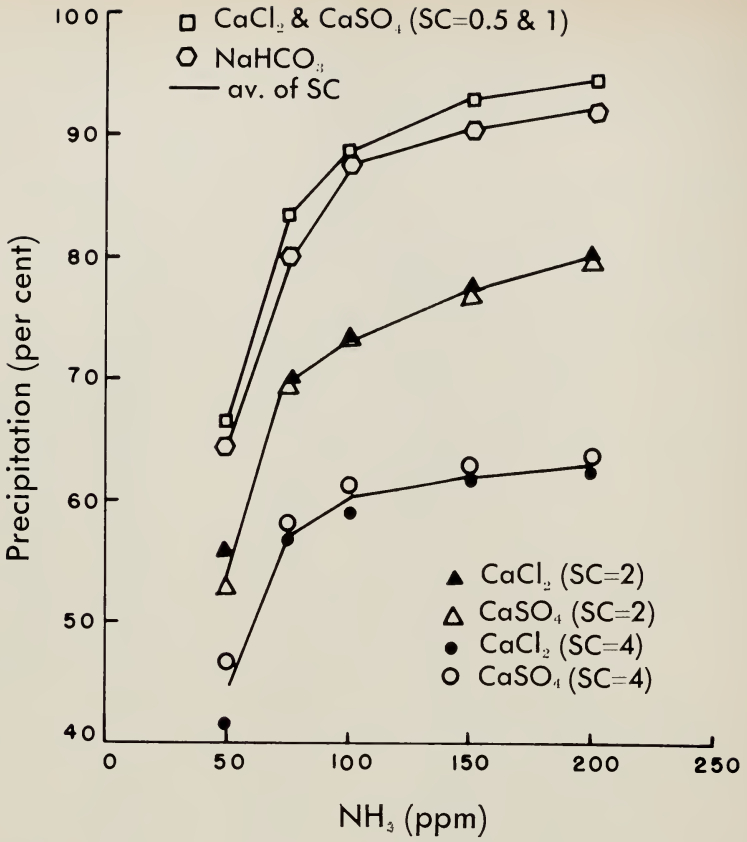


Fig. 10. Average percentage precipitation of total Ca^{++} as $CaCO_3$ in mixed salt solutions containing the common ion Ca^{++} of varying symmetry concentrations (SC).

with increasing NH_3 concentration in a given solution mixture. The particles were observed under 100 × magnification. The crystal forms of lime were identical in the NaCl and Na_2SO_4 systems. At low salt concentrations single crystals of rhombic calcite and dumbbell-shaped aragonite (Appendix fig. 3) were found in nearly equal proportions. But as the Na salt was increased to 2 symmetry concentration or greater, calcite was the predominant crystal, with some twinning of aragonite into pseudohexagonal forms. A smaller number of calcite aggregates—single crystals growing together at random—were observed. In the $NaHCO_3$ system, aragonite instead of calcite was the dominant crystal species. Dumbbell-shaped aragonite was preferentially formed over the pseudohexagonal forms.

At lower concentrations of $CaSO_4$ and $CaCl_2$, calcite and aragonite were found, with the former species in larger numbers. With concentration ratios of two or greater, aragonite was not present in these Ca salt systems. Prolific formation of large calcite crystals was observed, with a small number of acicular calcium carbonate hexahydrate and spherulitic calcium carbonate mono-

hydrate in the $CaSO_4$ and $CaCl_2$ systems, respectively.

At the lowest concentration of Mg salt, dumbbell-shaped aragonite predominated over the large but imperfectly developed calcite crystals. With a symmetry concentration of 1, a small number of ill-defined calcite crystals were found in the $MgCl_2$ system, but none in the $Mg(HCO_3)_2$. At greater concentrations of Mg^{++}, calcite was not present in either of these Mg systems, but a profuse growth of dumbbell-shaped aragonite plus some dark globular masses was observed in the $MgCl_2$ systems. In the corresponding $Mg(HCO_3)_2$ systems, aragonite was also found, but with needle-shaped crystals similar to the hexahydrate form, appearing singly and as aggregates.

The inhibiting effect of Mg on lime precipitation was determined in considering the gross precipitation of lime. However, the amount of Mg^{++} lost from these aqueous solutions was in trace amounts, and bore no relation to initial Mg^{++} concentrations. Apparently the presence of imperfectly developed calcite at the lower Mg^{++} concentrations indicates that distortion was due either to the replacement of Ca^{++} by the smaller Mg ion in the crystal lattice or the inclusion of magnesium carbonates. The hexahydrate-like crystals in the $Mg(HCO_3)_2$ system could not be positively identified because the ends of the needles were not pointed, as in the $CaSO_4$ system, but were almost square, with a columnar appearance. It is of interest to note that nesquehonite ($MgCO_3 \cdot 3H_2O$) commonly occurs as columnar needles. The formation of dark massive globs in the more concentrated $MgCl_2$ system was also not identified, but it appears to be similar to the gelatinous $Mg(OH)_2$ precipitated from a pure $Mg(OH)_2$ salt solution (Appendix fig. 3).

The crystals were re-examined after standing for two to four weeks in the stoppered flasks containing a thin film of solution. The hexahydrate and monohydrate forms of $CaCO_3$ were transformed into the more stable calcite and aragonite species. The globular mass in the $MgCl_2$ system and the columnar needles in the $Mg(HCO_3)_2$ were still present, but no change in size or number could be positively determined.

CONCLUSIONS ON AMMONIATED SOLUTIONS

The amount of NH_3 required to precipitate lime from a given salt solution depended largely upon the buffer capacity of the solution, provided Ca^{++} and HCO_3^- were not limiting. The buffer capacity of these solutions was related to the HCO_3^- content and pH.

The rate of crystallization of lime in a given salt solution was influenced by the degree of supersaturation attained with ammoniation. By lengthening the precipitation time, crystal sizes were increased for a given rate of NH_3, while increasing the NH_3 concentration resulted in a larger number of crystals and greater gross lime precipitation. The $CaCO_3$ crystals adhered strongly to glassware.

Increases in temperature enhanced lime precipitation between the 15 to 35° C range.

The solute species of Na^+, Cl^-, and

$SO_4^{=}$ had no influence on crystallization of lime in pure salt solutions.

The presence of Mg^{++} at lower concentrations inhibited precipitation and caused deformed calcite crystals. At higher concentrations it completely prevented calcite formation and instead, smaller quantities of metastable forms of lime were precipitated.

The addition of the common ion Ca^{++} promoted precipitation, but it was limited by the amount of HCO_3^- and aqueous CO_2 in the salt solutions used. The addition of the common ion HCO_3^- enhanced precipitation, but the buffer capacity of the solution was raised concurrently, and tended to offset the common-ion effect. When $Mg(HCO_3)_2$ was added to a $Ca(HCO_3)_2$ solution, the cumulative influence of the Mg inhibiting action and the increase in buffer capacity nearly counteracted the common-ion effect of the HCO_3^-.

LIME PRECIPITATION IN AMMONIATED NATURAL AND RECONSTITUTED WATERS

This phase of the investigation involved the testing of natural waters for their potential to precipitate lime. Appropriate amendments were added to waters deficient in the chemical constituents required for lime precipitation. The reconstituted waters are included in the tabulation of natural waters. The amendments used were $NaHCO_3$, $CaSO_4 \cdot 2H_2O$, and $CaCl_2$. The effects of common ion Ca^{++} and HCO_3^- are considered.

Also reported are additional studies made to determine the influence of particular chemical and physical factors on lime precipitation, including the inhibiting effect of Mg on precipitation, rates of gypsum dissolution, effect of dry salt admixtures, a comparison of $CaCl_2$ salt solution and solid $CaSO_4 \cdot 2H_2O$ amendments with respect to degree of precipitation, and adherence characteristics of the precipitate.

In an attempt to arrive at indices or parameters that predict lime precipitation qualitatively, if not quantitatively, several formulations were tested on the natural water data.

WATER CHARACTERISTICS

Representative surface and ground waters in California were surveyed for certain properties such as pH, Ca^{++}, HCO_3^-, and Mg^{++} contents (California State Department of Water Resources, 1964*a*,*b*). The range of natural water characteristics included in our investigation was partly drawn from that survey.

Because natural waters exist in a variety of solute combinations and concentrations it would be impractical to attempt to study all types of water. Instead, 83 waters, natural and reconstituted, were tested for lime precipitation. These are tabulated in Appendix C (pp. 48–49). Anyone wishing to test a water for lime-precipitation

potential may not always find a water in the Appendix table that exactly "matches" the one to be tested. It is important, therefore, to exercise caution when extrapolating between waters because of the complex relationships involved in lime chemistry. Most important of the variables is the inhibiting of lime formation by Mg.

Calcium content of the waters tested ranged from about 10 to 90 per cent of the total soluble cations, with the majority between 15 and 70 per cent. The concentration of Ca^{++} ranged from trace amounts to about 4 m.e. per liter. A few waters had higher concentrations. The survey of representative waters indicates pH values ranging from slightly below 7 to 8.5, with HCO_3^- concentrations up to 8 m.e. per liter. Our test waters contained a similar range of HCO_3^- but their pH was generally slightly higher because some of them were reconstituted with Ca^{++} and HCO_3^- amendments, which tended to increase pH. The partial pressure of CO_2 in typical California waters ranged from 1×10^{-2} to 2×10^{-4} atmospheres, whereas that in the test waters was between 5×10^{-3} and 2×10^{-5}. The HCO_3:Ca ratio in the test waters was nearly identical with that in the representative California waters, while the range of the Mg:Ca ratio was wider in test waters due to inclusion of waters specifically evaluated for the inhibiting effect of Mg^{++}.

Other constituents, such as Fe, Al, PO_4, and Si, which may form insoluble salts and minerals, were considered minor and relatively insignificant as compared with lime precipitation. In general, the test waters are typical of those found in California and the western United States, although a few odd types probably exist that are not encompassed in this study.

TESTING PROCEDURES

The potential of a given water for precipitating lime was tested by procedures outlined for 48-hour quiescent precipitation, with ammonia applied at rates of 50, 100, and 150 ppm.

Data confirming the approximation of quiescent 48-hour precipitation to the more dynamic six-hour precipitation and renewal cycles are given in table 4. The amount of lime precipitating from UC domestic water was very small, primarily because of the limited amount of Ca^{++}, whereas UC domestic water amended with gypsum yielded large amounts of precipitate. Under cyclic precipitation and renewal, the quantity of lime formed increased slightly with increasing cycles of six-hour precipitation. A favorable comparison is noted between the two very different precipitation conditions.

Before the present investigation was begun, additives such as CaO (burnt lime), $Ca(OH)_2$ (slaked lime), and NaOH (caustic soda) were tried, without success, for obtaining selective precipitation of lime from waters. In all cases precipitates other than $CaCO_3$, such as $Mg(OH)_2$ and $Ca(OH)_2$, were preferentially formed, a condition which at best only partly or temporarily sealed leaky pipes. These additives were too strongly alkaline or produced an alkaline condition, and were unsuitable as amendments. For this study, therefore, amendments were limited

TABLE 4

LIME PRECIPITATION IN UC DOMESTIC AND RECONSTITUTED AMMONIATED WATERS FOR 6-HOUR PRECIPITATION-RENEWAL CYCLES AND A 48-HOUR QUIESCENT PRECIPITATION PERIOD

Description	$CaCO_3$ precipitation in water treated with NH_3 at:		
	50 ppm	100 ppm	150 ppm
	m.e./l	*m.e./l*	*m.e./l*
UC domestic water*			
6-hr. cycles of precipitation and renwal:			
1st	0.05	0.08	0.10
2nd	0.10	0.13	0.18
3rd	0.10	0.14	0.18
4th	0.10	0.13	0.20
5th	0.12	0.17	0.25
6th	0.15	0.22	0.25
7th	0.14	0.19	0.27
8th	0.17	0.26	0.29
48-hr. quiescent precipitation	0.07	0.20	0.21
UC domestic water + 1.7 m.e./l $CaSO_4$			
6-hr. cycles of precipitation and renewal:			
1st	2.00	2.10	2.11
2nd	2.00	2.11	2.17
3rd	1.99	2.12	2.18
4th	1.99	2.15	2.17
5th	2.00	2.16	2.18
6th	2.00	2.16	2.17
7th	2.00	2.16	2.20
8th	2.01	2.17	2.21
48-hr. quiescent precipitation	2.15	2.28	2.32

* Composition (m.e. per liter): 0.86 Ca^{++}; 4.35 HCO_3^-; 1.29 Mg^{++}.

to NH_3, $CaSO_4 \cdot 2H_2O$, $CaCl_2$, and $NaHCO_3$.

Amendments added to waters that precipitated only small amounts of lime included $CaCl_2$ solution and solid-phase gypsum as sources for Ca^{++}, and $NaHCO_3$ salt or its solution as a source for HCO_3^-. The reconstituted waters were analyzed after addition of amendments and before ammoniation. For gypsum-treated waters, the salt was dissolved by stirring for several hours or more. Ammonia was then applied at appropriate rates. After 48 hours the treated waters were analyzed again, and the difference between initial and unprecipitated Ca^{++} was taken as the amount of lime precipitation. The reaction flasks were examined for identification of crystalline species of lime and other precipitates.

The Inhibiting Effect of Mg

For waters containing similar amounts of Ca^{++} and HCO_3^- a difference in Mg^{++} concentrations resulted in varying levels of lime precipitation. These findings confirm the previously reported inhibiting effect of Mg on lime formation in pure salt solutions (p. 11). Six groups of waters listed in table 5 illustrate the influence of Mg. In each group the Ca^{++} and HCO_3^- contents of the waters are nearly identical, but Mg^{++} is a variable. Within a group, an increase in Mg^{++} (and Mg:Ca ratio) resulted in a decrease in lime. Lime precipitation in this and following tables is reported in pounds of lime per acre-foot of water because encrustations of

TABLE 5

Mg INHIBITING EFFECT ON LIME PRECIPITATION IN AMMONIATED WATERS WITH SIMILAR Ca^{++} AND HCO_3^- CONTENTS

Water no.	Water composition*				$CaCO_3$ precipitation in water treated with NH_3 at:		
	Ca^{++}	HCO_3^-	Mg^{++}	Mg:Ca ratio	50 ppm	100 ppm	150 ppm
	m.e./l	*m.e./l*	*m.e./l*		*lb/acre-ft*	*lb/acre-ft*	*lb/acre-ft*
22	1.0	2.2	0.7	0.7	44	56	65
23	1.1	2.2	1.3	1.2	22	44	56
24	0.9	2.2	3.7	4.1	5	15	16
26	1.0	2.8	0.8	0.8	61	73	76
27	1.1	2.7	2.4	2.2	20	24	29
28	0.9	3.1	3.1	3.4	10	16	18
40	2.2	1.2	0.3	0.1	166	209	214
41	2.1	1.2	1.0	0.5	150	171	180
42	2.1	1.2	2.2	1.0	105	120	131
43	2.1	1.1	3.1	1.5	82	92	101
45	2.1	1.1	6.6	3.1	<1	3	8
52	2.3	2.2	0.6	0.3	253	268	273
47	2.1	2.1	1.2	0.6	190	214	218
34	1.9	2.0	2.2	1.2	128	154	159
35	1.9	2.0	4.2	2.2	46	91	106
48	2.2	1.9	8.3	3.8	31	34	41
60	2.8	1.1	0.4	0.1	197	222	231
56	2.7	1.1	1.7	0.6	116	159	196
57	2.6	1.1	4.0	1.5	110	136	173
71	3.7	1.1	0.4	0.1	237	318	320
72	3.6	1.1	2.6	0.7	173	209	155
73	3.6	1.1	5.2	1.4	156	182	138

* Complete analyses given in Appendix C.

lime in pipelines are usually evaluated on a weight basis and volume of water on an acre-foot basis may be readily converted to flow units.

The effect of Mg on lime precipitation makes predictions on the basis of present theories more difficult. Nevertheless, because this variable should be included in calculations, it was empirically considered as follows: Each water treated with 100-ppm NH_3 in a given group (table 5) was first evaluated in terms of fraction of initial Ca^{++} precipitated. This fractional precipitation value was then plotted against the Mg:Ca ratio of the water. A family of six curves representing the six groups of water was obtained. Each of the curves was then extended to a Mg:Ca ratio equal to zero. The intersection of the curves with the *y*-axis then gave an estimate of the fraction of Ca^{++} that may precipitate in the absence of Mg^{++}. The waters in each group were then re-evaluated in terms of the fraction of Ca^{++} precipitated relative to the estimated fractional precipitation without Mg^{++}. These new values were then plotted against the Mg:Ca ratio of the waters, and a single curve was obtained (fig. 11). From this relationship it is now possible to estimate quantitatively the influence of Mg on lime precipitation. For example, the estimated precipitation in a water having a Mg:Ca ratio of 2.0 is only 37 per cent of the

TABLE 6

EFFECT OF COMMON ION Ca^{++} ON LIME PRECIPITATION IN AMMONIATED WATERS WITH SIMILAR HCO_3^- AND Mg^{++} CONTENTS

Water no.	Water composition*				$CaCO_3$ precipitation in water treated with NH_3 at:		
	HCO_3^-	Mg^{++}	Ca^{++}	Mg:Ca ratio	50 ppm	100 ppm	150 ppm
	m.e./l	*m.e./l*	*m.e./l*		*lb/acre-ft*	*lb/acre-ft*	*lb/acre-ft*
2	1.2	0.3	0.2	1.5	5	5	5
16	1.1	0.4	0.8	0.5	7	20	27
30	1.2	0.3	1.3	0.23	69	106	110
33	1.0	0.4	1.9	0.21	114	148	171
40	1.2	0.3	2.2	0.14	116	209	214
60	1.1	0.4	2.8	0.14	197	222	231
71	1.1	0.4	3.7	0.11	237	318	320
10	2.1	0.6	0.4	1.5	1	1	1
79	2.1	0.6	4.3	0.1	416	471	487
11	2.1	1.3	0.6	2.2	7	8	10
23	2.2	1.3	1.1	1.2	22	44	56
47	2.1	1.2	2.1	0.6	190	214	218
34	2.0	2.2	1.9	1.2	128	154	159
62	2.0	2.2	3.0	0.7	207	261	279
20	4.4	1.3	0.9	1.4	14	15	27
36	4.2	1.3	1.8	0.7	158	174	181
59	4.4	1.4	2.6	0.5	286	298	301
76	4.2	1.3	3.8	0.3	432	469	471

* Complete analyses given in Appendix C.

lime that would precipitate from a similar water that is free of Mg^{++}. (In a later section (p. 42) the empirically derived inhibiting factor is applied to natural waters treated with 100 ppm NH_3.)

Effect of Common Ion Ca^{++} or HCO_3^-

The common-ion Ca^{++} effect in waters containing similar HCO_3^- and Mg^{++} concentrations is illustrated in table 6. Large amounts of lime are precipitated by increasing Ca^{++}. In addition to the common-ion effect, the Mg:Ca ratio is concurrently reduced. These two factors are not readily separable. The result of these effects—Mg inhibiting of lime precipitation—can be partly overcome by Ca^{++} amendments.

An analogous condition is obtained with HCO_3^- as the common ion (table 7). The net effect of common ion HCO_3^- is somewhat less significant than that of Ca^{++} for several reasons. The Mg:Ca

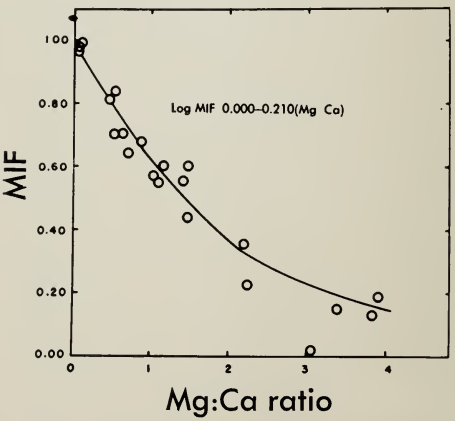


Fig. 11. Relation between Mg inhibiting factor (MIF) and Mg:Ca ratio of waters listed in table 5. The MIF is defined as the fraction of $CaCO_3$ that precipitates at a given Mg:Ca ratio as compared with that of a similar water free of Mg^{++}.

TABLE 7

EFFECT OF COMMON ION HCO_3^- ON LIME PRECIPITATION IN AMMONIATED WATERS WITH SIMILAR Ca^{++} AND Mg^{++} CONTENTS

Water no.	Water composition*				$CaCO_3$ precipitation in water treated with NH_3 at:		
	Ca^{++}	Mg^{++}	HCO_3^-	HCO_3:Ca ratio	50 ppm	100 ppm	150 ppm
	m.e./l	*m.e./l*	*m.e./l*		*lb/acre-ft*	*lb/acre-ft*	*lb/acre-ft*
15	1.0	0.8	0.7	0.7	<1	3	3
21	1.1	0.7	1.8	1.6	18	20	24
22	1.0	0.7	2.2	2.2	44	56	65
25	1.0	0.7	2.8	2.8	92	105	109
29	1.0	0.7	3.8	3.8	110	118	122
39	2.2	0.2	0.7	0.3	109	131	152
40	2.2	0.3	1.2	0.5	166	209	214
51	2.4	0.2	1.6	0.7	252	273	283
54	2.3	0.2	2.5	1.1	268	279	284
55	2.3	0.2	3.3	1.4	286	292	296
62	3.0	2.2	2.0	0.7	207	261	279
63	2.8	2.3	3.0	1.1	275	330	335
70	3.2	2.1	5.6	1.8	324	367	374

* Complete analyses given in Appendix C.

TABLE 8

PRECIPITATION OF LIME IN ORIGINAL AND RECONSTITUTED (WITH CALCIUM AMENDMENTS) AMMONIATED WATERS

Water no.	Water composition*			$CaCO_3$ precipitation in water treated with NH_3 at:		
	Ca^{++}	HCO_3^-	Mg:Ca ratio	50 ppm	100 ppm	150 ppm
	m.e./l	*m.e./l*		*lb/acre-ft*	*lb/acre-ft*	*lb/acre-ft*
4	0.2	1.1	1.6	1	3	3
41†	2.1	1.2	0.5	150	171	180
9	0.4	2.1	1.4	3	4	5
52†	2.3	2.1	0.3	253	268	273
12	0.5	2.9	1.6	5	8	8
26‡	1.0	2.8	0.9	61	73	76
17	0.8	1.1	1.6	1	7	15
56‡	2.7	1.1	0.6	110	159	196
24	0.9	2.2	3.9	5	15	16
53‡	2.4	2.1	1.6	182	238	253
31	1.3	2.3	0.4	87	97	114
61‡	3.0	2.3	0.2	290	328	337
37	1.9	8.0	2.8	109	150	150
78†	3.8	7.8	1.5	298	426	447
59	2.1	4.1	1.2	180	185	192
64‡	2.9	4.1	1.0	298	310	321
62	3.0	2.0	0.7	207	261	279
81†	5.6	2.0	0.5	396	432	450

* Complete analyses given in Appendix C.
† Water + $CaSO_4$.
‡ Water + $CaCl_2$.

ratio is unaffected and only the HCO_3:Ca ratio is increased. The added HCO_3^- contributes to the buffer capacity of the water. Moreover, comparison should be made between Ca^{++} and $CO_3^=$, derived primarily through ammoniation, and not with HCO_3^-. Thus the magnitude of the common-ion HCO_3^- effect is generally less than that of the common ion Ca^{++}.

Reconstituted Waters

Waters lacking sufficient Ca^{++} for maximum precipitation (table 8) received either gypsum or $CaCl_2$ as an amendment. The dual effect of common ion Ca^{++} and reduction in Mg:Ca ratio increased precipitation substantially. Certain waters that precipitated appreciable amounts of lime (for example waters 37, 50, and 62) were also treated with calcium additives, and still larger amounts of lime were produced.

Waters deficient in HCO_3^- were reconstituted with $NaHCO_3$ salt solutions. The impact of common ion HCO_3^- was less than that of the Ca^{++} ion (table 9). Admixtures of $NaHCO_3$ and $CaSO_4$ amendments were applied to waters containing limiting concentrations of both HCO_3^- and Ca^{++}. The addition of only $NaHCO_3$ to water 5 resulted in a small amount of precipitate, but when both $NaHCO_3$ and $CaSO_4$ were added (water 54), the amount of lime was greatly increased (table 9). Similar results were obtained with water 16 and its reconstituted waters, 19 and 67. If Ca^{++} is not limiting (water 17), the addition of HCO_3^- provides substantial gains in the amount of precipitation.

TABLE 9

PRECIPITATION OF LIME IN ORIGINAL AND RECONSTITUTED (WITH BICARBONATE AND BICARBONATE-CALCIUM AMENDMENTS) AMMONIATED WATERS

Water no.	Water composition*			$CaCO_3$ precipitation in water treated with NH_3 at:		
	Ca^{++}	HCO_3^-	Mg:Ca ratio	50 ppm	100 ppm	150 ppm
	m.e./l	*m.e./l*		*lb/acre-ft*	*lb/acre-ft*	*lb/acre-ft*
5	0.4	0.6	0.4	7	7	7
8†	0.4	2.1	0.5	33	38	44
5	0.4	0.6	0.4	7	7	7
54‡	2.3	2.5	0.1	268	279	284
7	0.4	0.6	2.3	4	8	8
58‡	2.5	2.8	0.5	271	284	295
16	0.8	1.1	0.5	7	20	27
19†	0.9	4.1	0.5	98	103	105
16	0.8	1.1	0.5	7	20	27
67‡	3.3	3.7	<0.1	412	426	428
31	1.3	2.3	0.4	87	97	114
49‡	2.1	3.2	0.3	231	248	252
17	2.2	0.7	0.1	109	131	152
55†	2.3	3.3	<0.1	286	292	296

* Complete analyses given in Appendix C.
† Water + $NaHCO_3$.
‡ Water + $NaHCO_3$ + $CaSO_4$.

Nature of Precipitates

The precipitates formed in the test waters were examined under 100× magnification. A variety of crystalline species of lime was produced. Vaterite, calcite, and aragonite (Appendix fig. 3) were the most common forms. Infrequently, $CaCO_3 \cdot 6H_2O$ and $CaCO_3 \cdot H_2O$ were observed in ammoniated waters. For many waters yielding relatively small amounts of lime because of high Mg^{++} content, the crystalline species observed were ill-defined and often appeared as globular masses of a colloidal or gel-like nature. The predominant crystalline species produced by solutes or amendments were:

Amendments	Predominant Crystalline Species
$NaHCO_3$	aragonite
$NaHCO_3 + CaCl_2$	aragonite, calcite
$NaHCO_3 + CaSO_4$	aragonite, calcite
$CaSO_4$ (low Mg^{++})	calcite
$CaSO_4$ (moderate Mg^{++})	vaterite, calcite
$CaSO_4$ (high Mg^{++})	aragonite, vaterite
$CaCl_2$	calcite, aragonite
$CaCl_2$ (Mg^{++})	vaterite, calcite

Although exceptions were noted, these observations are in general agreement with those of other investigators (Johnston, Merwin, and Williamson, 1916; Brooks, Clark, and Thurston, 1950; Buehrer and Reitemeir, 1940).

The rate of nucleation and crystal growth in the test waters was generally slow, and all of the readily identifiable crystalline forms of lime adhered tenaciously to the surface of the glassware. But where precipitation was instantaneous, upon ammoniation, the precipitants were of colloidal sizes and appeared as minute dots at 100× magnification. Under these spontaneous precipitation conditions the precipitates tended to be softer and loose, especially with some of the highest concentrations of gypsum amendments (waters 79, 81, 82, 83, Appendix C). (Suspended and adhered precipitates are discussed in more detail on p. 31.)

Table 10

COPRECIPITATION OF Mg^{++} IN AMMONIATED WATERS, CALCULATED $Mg(OH)_2$ PRECIPITATION, AND OTHER PARAMETERS

Water no.	Mg^{++} precipitation in water treated with NH_3 at:			Water treated with 100 ppm NH_3					
	50 ppm	100 ppm	150 ppm	Calc. $Mg(OH)_2$	Initial Mg^{++}	Initial Mg:Ca ratio	Final Mg:Ca ratio	Super-saturation ratio	Mg:Ca precipitation ratio
	m.e./l	*m.e./l*	*m.e./l*	*m.e./l*	*m.e./l*				
83	0.70	0.74	0.74	0.51	2.9	0.4	0.4	11.7	0.22
78	0.57	0.75	0.74	0.74	5.6	1.5	7.6	18.2	0.24
68	0.71	0.66	0.68	0.77	4.8	1.5	14.9	13.4	0.23
81	0.63	0.60	0.60	0.50	2.7	0.5	0.9	10.2	0.19
64	0.35	0.52	0.50	0.50	2.8	1.0	3.5	13.0	0.23
69	0.37	0.52	0.37	0.74	5.5	1.6	6.1	12.9	0.20
37	0.40	0.44	0.52	0.75	5.4	2.8	6.1	13.8	0.40
65	0.26	0.39	0.34	0.72	5.5	2.0	7.2	17.7	0.19
61	0.30	0.33	0.32	0.29	0.6	0.2	0.8	8.6	0.14
71	0.29	0.33	0.31	0.33	0.7	0.7	0.8	5.4	0.46
59	0.25	0.32	0.34	0.44	1.3	0.5	2.6	12.7	0.15
75	0.20	0.27	0.25	0.49	2.4	0.6	1.6	8.9	0.11
50	0.13	0.25	0.27	0.50	2.6	1.2	3.0	11.2	0.18
79	0.14	0.19	0.20	0.30	0.6	0.1	0.5	10.0	0.05
49	0.21	0.19	0.11	0.31	0.7	0.3	1.6	8.8	0.10
36	0.20	0.18	0.17	0.43	1.3	0.7	2.3	10.4	0.14
63	0.18	0.17	0.22	0.50	2.3	0.8	5.8	9.5	0.07

Coprecipitation of Magnesium

In general, only trace amounts of Mg^{++} were precipitated from ammoniated waters, with the exception of the waters listed in table 10. The mechanism(s) by which Mg^{++} coprecipitates in these waters is not fully known. The degree of coprecipitation was not related to initial Mg^{++} concentration or initial Mg:Ca ratio. Only trace amounts precipitated from other waters having similar or higher Mg^{++} contents or Mg:Ca ratios. Magnesium precipitation is also not related to the final Mg:Ca ratio—i.e., after lime precipitation—nor is it related to the initial or final pH of the waters. The supersaturation ratio (defined by equation [19], Appendix A) is related to rate of nucleation and crystal growth—the higher its value the greater the chance for Mg^{++} being occluded or entrapped in the precipitating lime. Apparently, coprecipitation is not significantly correlated to the supersaturation ratio (table 10) or the Mg:Ca precipitation ratio.

ACTION OF AMENDMENTS UNDER SIMULATED FIELD CONDITIONS

In the procedures adopted to test natural and reconstituted waters, $CaCl_2$ and $NaHCO_3$ were added as liquids and $CaSO_4$ was added as a solid, but dissolved before ammoniation, to simulate introduction of amendments upstream in relation to the NH_3 injection site. The tests were carried out under a 48-hour quiescent precipitation period. The effect of applying $CaSO_4$ and/or $NaHCO_3$ in the dry state, with gypsum applicators and other similar devices, at the site of NH_3 injection or just upstream was explored. These and other related studies were carried out under simulated field conditions, e.g., with stirring or agitation.

Dissolution Rate of Gypsum

The solubility of gypsum is affected by temperature, but the concentration required to provide sufficient Ca^{++} to precipitate lime in waters is about one-tenth its solubility. The rate of gypsum dissolution in waters is more important. Powder-form gypsum at concentrations of 3 and 5 m.e. per liter was added to CO_2-free distilled water, and the reaction flask was placed on a shaker. The horizontal shaking machine was set at 60 oscillations (1-inch strokes) per minute to simulate agitation not too different from flow of water through pipelines. The dissolution rate of gypsum was determined for 5 to 60 minutes of elapsed time by analysis for supernatant Ca^{++}. The ratio of supernatant Ca^{++} to added $CaSO_4$ provided a measure of dissolution (fig. 12). Within 20 minutes, more than 95 per cent of the added gypsum was dissolved. The difference in rate of dissolution between 3 and 5 m.e. per liter of added gypsum is relatively small. Gypsum in granulated form has a lower dissolution rate.

Putah South Canal water contains sufficient HCO_3^- and 0.4 m.e. per liter of $CO_3^=$ but insufficient Ca^{++} for substantial lime precipitation. Gypsum was added to this nonammoniated water at rates of 4 and 6 m.e. per liter. The flasks were placed on a shaker and the waters were analyzed at periods from 15 minutes to 6 hours. Within 15 minutes most of the gypsum had dissolved (table 11), and apparently solubilization increased only slightly for the remaining period. Calcium in the solid

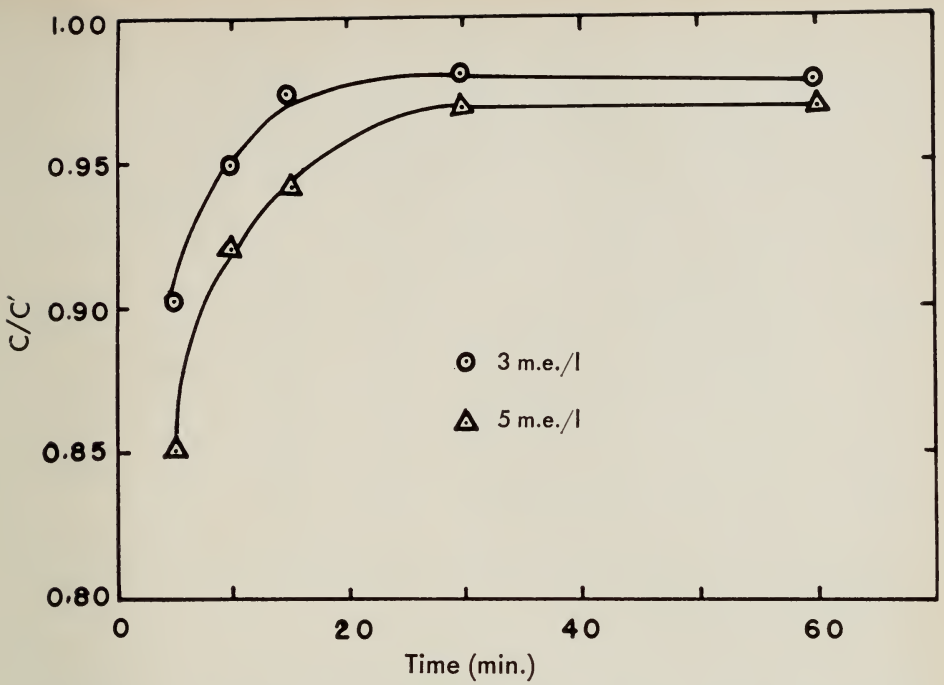


Fig. 12. Dissolution rate of gypsum (CP grade, powder form) in CO_2-free distilled water for 3 and 5 m.e. liter of added gypsum. C = supernatant Ca^{++} and C′ = added $CaSO_4$ concentration.

form consists of undissolved gypsum and/or precipitated lime. These results indicate that when an excess of calcium amendment is added to a water containing some $CO_3^{=}$, only a small amount of lime precipitates because NH_3 is required to convert HCO_3^- to $CO_3^{=}$.

Dry Salt Mixtures as Amendments

The addition of dry salt mixtures of $CaSO_4$ and $NaHCO_3$ to waters deficient in both Ca^{++} and HCO_3^- by means of gypsum applicators and other devices is a possibility. Gypsum in a powdered form is not entirely compat-

TABLE 11

SOLUBILITY OF GYPSUM OVER VARIOUS PERIODS OF TIME IN NONAMMONIATED WATER FROM PUTAH SOUTH CANAL*

Solubilization period	Water + 4 m.e./l $CaSO_4$			Water + 6 m.e./l $CaSO_4$		
	Soluble Ca^{++}	Solid† Ca	pH	Soluble Ca^{++}	Solid† Ca	pH
hrs	*m.e./l*	*m.e./l*		*m.e./l*	*m.e./l*	
0.25	4.50	0.38	8.74	6.50	0.38	8.68
0.5	4.56	0.32	8.73	6.52	0.36	8.66
1.0	4.63	0.25	8.71	6.63	0.25	8.67
3.0	4.69	0.19	8.72	6.63	0.25	8.65
6.0	4.70	0.18	8.71	6.72	0.16	8.64

* Analysis for water No. 18 given in Appendix C.
† Solid Ca consists of gypsum that was not completely dissolved, and any precipitated lime.

Table 12

LIME PRECIPITATION IN WATER FROM THE PUTAH SOUTH CANAL AND THE SACRAMENTO RIVER, FOLLOWING ADDITION OF 100 PPM NH_3 AND SEVERAL RATES OF GYPSUM OR DRY SALT MIXTURES ($CaSO_4$:$NaHCO_3$)
(Precipitation periods, 6 hours and 3 hours, respectively)

Water	Amendments	Ca^{++}	pH†	$CaCO_3$ precipitation‡	
		m.e./l		*m.e./l*	*lb/acre-ft*
Putah South Canal*	untreated	0.88	8.47	....	...
	2 m.e./l $CaSO_4$	0.77	9.67	2.11	287
	4 m.e./l $CaSO_4$	1.13	9.58	3.75	510
	6 m.e./l $CaSO_4$	2.18	9.48	4.70	639
	2 m.e./l $CaSO_4$ + 1 m.e./l $NaHCO_3$	0.65	9.74	2.23	363
	4 m.e./l $CaSO_4$ + 2 m.e./l $NaHCO_3$	0.73	9.45	4.15	564
	6 m.e./l $CaSO_4$ + 3 m.e./l $NaHCO_3$	0.80	9.31	6.08	827
Sacramento River§	untreated	0.89	7.85	....	...
	2 m.e./l $CaSO_4$ + 2 m.e./l $NaHCO_3$	0.24	9.65	2.65	360
	4 m.e./l $CaSO_4$ + 4 m.e./l $NaHCO_3$	0.33	9.27	4.56	620
	6 m.e./l $CaSO_4$ + 6 m.e./l $NaHCO_3$	0.36	9.14	6.53	888

* Contains 2.03 m.e./l Mg^{++}, 2.63 m.e./l HCO_3^-, 0.39 m.e./l $CO_3^=$.
† Ca^{++} concentration and pH at end of precipitation period.
‡ Includes suspended precipitates.
§ Contains 0.42 m.e./l Mg^{++}, 1.04 m.e./l HCO_3^-.

ible for mixing with granular $NaHCO_3$ salt. A combination of these dry salts is similar to a mixture of flour and common table salt. Dry mixes of gypsum and $NaHCO_3$, and gypsum alone, were added to Putah South Canal and Sacramento River waters, followed immediately by 100 ppm NH_3 for 6 and 3 hours of shaking, respectively (table 12). Amendments were added in excess to determine the upper limits of applications with respect to the desired type of lime precipitation, and the effects of adding solid amendments at the same site used for injection of anhydrous NH_3.

The application of dry salt amendments to the waters produced a cloudy suspension that slowly began to clarify, but before complete dissolution occurred, NH_3 was introduced. As NH_3 came into contact with the water, very fine suspended material began to form. In fact, both dissolution of amendment and precipitation of lime appeared to be taking place simultaneously. At added gypsum and/or gypsum + $NaHCO_3$ concentrations of 4 m.e. per liter or greater, the precipitation was spontaneous, and resulted in a loose accumulation of colloidal material in the bottoms of the flasks. The amount of precipitate adhering to the glassware after decantation appeared to be the same regardless of the amount of precipitation taking place. Following acid treatment, both the adhered and suspended material effervesced vigorously, a positive test for $CaCO_3$. These observations indicate that an excess of either amendment or dry mixes of gypsum and $NaHCO_3$ is undesirable for sealing operations. Furthermore, NH_3 and dry salts or a mixture of dry amendments should not be added at the same location.

$CaCl_2$ Solution as an Amendment

Because of the problems with the solubility of gypsum mentioned above, $CaCl_2$ as an amendment was investigated. This deliquescent salt is ex-

TABLE 13

LIME PRECIPITATION IN AMMONIATED WATER (100 PPM NH_3) WITH ADDED $CaCl_2$ SALT SOLUTION

(6-hour precipitation period on a mechanical shaker)

Water characteristics					$CaCO_3$ precipitation	
Amendments		Ca^{++}	$Ca:HCO_3$ ratio	$Mg:Ca$ ratio	$CaCO_3$	Adhered $CaCO_3$
Water	Added $CaCl_2$					
	m.e./l	*m.e./l*			*m.e./l*	*per cent*
A*	0	2.0	0.25	2.7	0.50	96
A	0	4.0	0.50	1.4	2.80	100
A	4	6.0	0.75	0.9	4.65	93
A	6	8.0	1.00	0.7	6.13	100
B†	0	1.0	0.25	2.7	0.01	100
B	1	2.0	0.50	1.4	0.86	98
B	2	3.0	0.75	0.9	1.89	100
B	3	4.0	1.00	0.7	2.68	97

* Contains 8 m.e./l HCO_3^- and 5.4 m.e./l Mg^{++}.
† Water A diluted twofold with distilled water.

tremely difficult to handle in the dry state, and would probably be applied to the irrigation water either in solution, or as a brine. Solubility would not be a problem and only sufficient agitation for mixing would be required. Experimental water A contained 8 m.e. of HCO_3^- and 2 m.e. per liter of Ca^{++}. These concentrations will form about 150 pounds of lime per acre-foot of water, but because of Mg interference, only 68 pounds of lime were precipitated when 100 ppm NH_3 were added. Adding $CaCl_2$ greatly increased precipitation (table 13) by overcoming the inhibiting effect of Mg and by increasing the common ion Ca^{++}. Water B was prepared by diluting water A with distilled water in equal proportions. The addition of $CaCl_2$ amendment to water B increased precipitation of lime from 0.01 to 2.68 m.e. per liter over a 6-hour agitation period.

The added concentrations of $CaCl_2$ brought about an approximately linear increase in lime precipitation. The lime formed in these waters adhered strongly to glassware (table 13), and the precipitates crystallized up to the water line in the flasks. The adhered portion of lime was not dislodged by a direct stream of water.

Dry and Liquid Amendments

A water deficient in both Ca^{++} and HCO_3^- was tested by introducing NH_3 immediately after the solid $CaSO_4$-$NaHCO_3$ mixture was added. In all combinations of equal concentration the total amount of lime formed was slightly larger with the $CaSO_4$-$NaHCO_3$ than with the $CaCl_2$-$NaHCO_3$ treatments. But as the $CaSO_4$-$NaHCO_3$ mixture increased in concentration above 1 m.e. per liter, large amounts of "soft" lime were produced, with a corresponding decrease in the percentage adhering to the glassware as "hard" lime (table 14).

Because solid $NaHCO_3$ is readily soluble in the amounts added, and the $CaCl_2$ was in the liquid form, nearly complete dissolution was attained before the addition of NH_3. Consequently,

TABLE 14

COMPARISON OF SOLID $CaSO_4$ + $NaHCO_3$ AND LIQUID $CaCl_2$ + $NaHCO_3$ AMENDMENTS IN SACRAMENTO RIVER WATER TREATED WITH 100 PPM NH_3

Ca:HCO_3 ratio	Amendments			$CaCO_3$ precipitation	Per cent of total $CaCO_3$ adhered* to glass
	$CaSO_4$	$CaCl_2$	$NaHCO_3$		
	m.e./l	*m.e./l*	*m.e./l*	*m.e./l*	
1:1	+1		+1	1.47	86
		+1	+1	1.32	100
	+2		+2	2.47	49
		+2	+2	2.17	100
	+3		+3	3.47	22
		+3	+3	3.26	100
	+4		+4	4.49	15
		+4	+4	4.21	100
2:1	+2		+1	2.33	59
		+2	+1	1.89	100
	+4		+2	4.37	26
		+4	+2	3.46	100
1:2	+1		+2	1.56	72
		+1	+2	1.29	100
	+2		+4	2.57	51
		+2	+4	2.50	99
3:1	+3		+1	2.98	42
		+3	+1	2.48	100
	+6		+2	5.02	11
		+6	+2	4.64	95
1:3	+1		+3	1.59	54
		+1	+3	1.49	100
	+2		+6	2.58	33
		+2	+6	2.45	93

* Refers to lime clinging to reaction flask after washing with a stream of water.

100 per cent of the precipitate adhered to the reaction flask, except at the higher concentrations, in which over 90 per cent was hard lime. These crystals were readily identified as calcite, aragonite, and vaterite.

The soft precipitate formed from the $CaSO_4$-$NaHCO_3$ mixture appeared as minute dots at 100× magnification. Whether this precipitate was microcrystalline or noncrystalline is not important, but it is significant that the material was loose and did not grow nor crystallize into hard lime even with age.

If a dry amendment is to be used, it is essential that the amendment be completely dissolved in the flowing water before introduction of NH_3; otherwise high concentrations of Ca^{++} and/or $CO_3^{=}$ will occur at or near the surface of the dissolving particles, resulting in spontaneous precipitation. Therefore, under field conditions it will be necessary to introduce gypsum sufficiently in advance of NH_3 injection, to allow for dissolution. And if $NaHCO_3$ is also used, it should be added separately with proper spacing between gypsum, $NaHCO_3$, and NH_3 introductions. Under most conditions, $NaHCO_3$ will dissolve at a faster rate than gypsum.

A rigid control in the continuous addition of amendments, NH_3, and flow of water must be maintained to obtain the desired concentration for maximum precipitation of hard or crystalline lime. Ammonia should be applied at a concentration rate of about 100 ppm for most waters, and the treated water should be in contact with the pipeline for 6 hours or more.

Additional information on field techniques for sealing concrete pipelines are given in another paper (Tanji *et al.*, 1968).

APPENDIX A: THEORETICAL CONSIDERATIONS

The chemistry involved in the ammoniation of waters for precipitating lime is extremely complex. The system includes the interaction between a weak acid (carbonic) and a weak base (ammonia), coupled with the solubility of lime. The precipitants must be crystalline, with adherence properties, rather than suspended or gelatinous—characteristics which may lead to only temporary mechanical sealing. Furthermore, natural waters contain other dissolved salts which may affect crystallization of lime and may even precipitate. Therefore, the sealing of leaks in concrete pipelines by ammonia treatment of waters passing through them requires certain chemical and physical conditions for successful operation.

CHEMICAL EQUILIBRIA FOR LIME AND AMMONIA

NH_3–H_2O System

The equilibria for NH_3 in water may be described as

$$NH_3\ (\text{gas}) \rightleftarrows NH_3\ (\text{aqueous}) \qquad [1]$$

$$NH_3\ (\text{aqueous}) + H_2O \rightleftarrows NH_4OH \rightleftarrows NH_4^+ + OH^- \qquad [2]$$

The dissociation constant of aqueous NH_3, K_b, is defined by

$$K_b = \frac{[NH_4^+]\,[OH^-]}{[NH_3]\,[H_2O]} = \frac{[NH_4^+]\,[OH^-]}{C_{NH_3}\,P_{NH_3}} \qquad [3]$$

where brackets denote activities which in very dilute solutions are approximately equal to the molar concentration, C_{NH_3} is the molar concentration (27.6) of dissolved ammonia at standard temperature and pressure (Washburn, 1928), P_{NH_3} is the partial pressure of NH_3 in atmospheres, and K_b has a value of 1.77×10^{-5} (Hodgman, 1955) at 25° C. The $[NH_3]$ is taken to include aqueous NH_3 and NH_4OH. Water has a relatively high affinity for NH_3 gas, but at a given partial pressure C_{NH_3} decreases exponentially with increases in temperature. Although K_b increases parabolically with temperature, the dissociation of aqueous NH_3 into NH_4^+ and OH^- is relatively low.

The CO_2-H_2O system is described by

$$CO_2 \text{ (gas)} \rightleftarrows CO_2 \text{ (aqueous)} \quad [4]$$

$$CO_2 \text{ (aqueous)} + H_2O \rightleftarrows H_2CO_3 \rightleftarrows H^+ + HCO_3^- \quad [5]$$

and

$$HCO_3^- \rightleftarrows H^+ + CO_3^= \quad [6]$$

The first and second ionization constants, K_1 and K_2, of carbonic acid are

$$K_1 = \frac{[HCO_3^-]\,[H^+]}{[CO_2]\,[H_2O]} = \frac{[HCO_3^-]\,[H^+]}{C_{CO_2} P_{CO_2}} \quad [7]$$

$$K_2 = \frac{[CO_3^=]\,[H^+]}{[HCO_3^-]} \quad [8]$$

where brackets denote activities, C_{CO_2} is the molar concentration (3.8×10^{-2}) of dissolved CO_2 gas at standard temperature and pressure (Johnston, 1915), and P_{CO_2} is the partial pressure of CO_2 in atmospheres. Values reported for K_1 and K_2 at 25° C are 4.45×10^{-7} (Harned and Davis, 1943) and 4.69×10^{-11} (Harned and Scholes, 1941), respectively. By convention $[CO_2]$ is the sum of H_2CO_3 and dissolved CO_2. For a given partial pressure, CO_2 gas dissolves in water in much smaller amounts than does NH_3. Both K_1 and K_2 increase almost linearly with rise in temperature, but the ionization of aqueous CO_2 to HCO_3^- and $CO_3^=$ is low.

The fractional species of carbonic acid as related to pH is illustrated in Appendix figure 1 for CO_2-H_2O system at 25° C. Theoretically, the pH of a CO_2-H_2O system must have a value of pH 8.35 for $CO_3^=$ to be present. Consequently the pH of a HCO_3^- water should be raised to greater than 8.35 for precipitation of $CaCO_3$.

The solubility of lime is defined by

$$K_{CaCO_3} = [Ca^{++}]\,[CO_3^=] \quad [9]$$

Where K_{CaCO_3} is the solubility-product constant (4.82×10^{-9}) for calcite (Frear and Johnston, 1929). Replacing $[CO_3^=]$ in equation [9] by [8] and subsequently substituting $[HCO_3^-]$ from equation [7] yields

$$K_{CaCO_3} = \frac{[Ca^{++}] C_{CO_2} P_{CO_2} K_1 K_2}{[H^+]^2} \quad [10]$$

The integration of the carbonic acid equilibria into the solubility-product constant of calcite defines the interrelations of P_{CO_2}, pH, and Ca^{++}. A comprehensive method for predicting the solubility and precipitation of $CaCO_3$ in mixed systems has been formulated for computer programming by Tanji and Doneen (1966*a*).

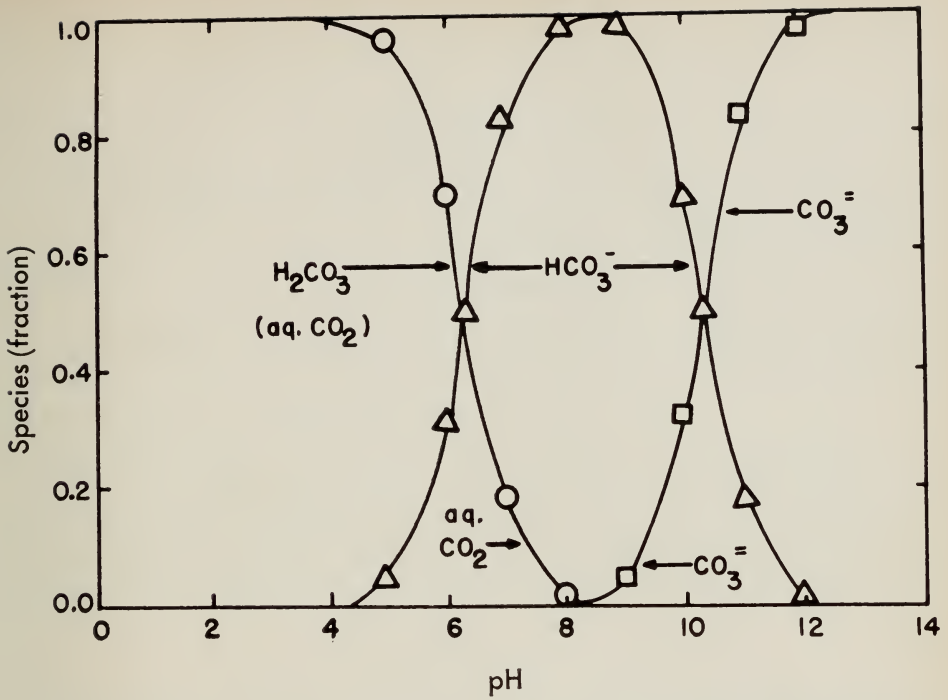


Fig. 1A. Distribution of carbonic acid species as related to pH, for CO_2-H_2O system at 25° C.

NH_3–$CaCO_3$–H_2O System

Information on the NH_3-$CaCO_3$ system is very meager and only a few studies have been reported (Weir, 1957; Reitemeir and Buehrer, 1940; Reitemeir, 1940). The conversion of HCO_3^- to $CO_3^=$ is the key step for the formation of $CaCO_3$ in waters. The addition of a base to a HCO_3^- water would tend to shift the following reaction to the right.

$$HCO_3^- + OH^- \rightleftarrows CO_3^= + H_2O \qquad [11]$$

The introduction of a strong base, such as NaOH or KOH, to a weakly buffered HCO_3^- solution leads to large increases in pH. In the presence of appreciable amounts of OH^-, salts with a lower solubility than calcite tend to precipitate. Some of these salts precipitate in a noncrystalline form and lack the adherence properties of calcite. One such gel-like precipitate is $Mg(OH)_2$ with a solubility-product constant of 5.0×10^{-12} (Kline, 1929). Therefore the amount and kind of base added to a water of a given composition are important. Since Mg^{++} is a natural constituent of waters, the pH of the water should not be raised to extreme alkaline ranges. When Ca^{++} and HCO_3^- are in sufficient concentrations, the use of a weak base such as aqueous NH_3 would cause relatively smaller pH changes, resulting in the selective precipitation of $CaCO_3$.

The equilibrium constant for the reaction, equation [11], is

$$K_e = \frac{[CO_3^{=}]}{[HCO_3^{-}]\,[OH^{-}]} \qquad [12]$$

where K_e is equivalent to K_2/K_w or 4.69×10^3. And the momentary $CO_3^{=}$ concentration resulting from this reaction is

$$[CO_3^{=}] = K_e\,[HCO_3^{-}]\,[OH^{-}] \qquad [13]$$

Substituting $[OH^{-}]$ from [3], equation [13] becomes

$$[CO_3^{=}] = K_e\,[HCO_3^{-}](K_b[NH_4OH])^{1/2} \qquad [14]$$

To represent stoichiometric aqueous NH_3 concentration the symbol NH_4OH is used, recognizing that aqueous NH_3 exists as $NH_{3(aq)}$ and NH_4^{+}.

Since K_2, equation [8], is much smaller than K_e, equation [12], the principal source of $CO_3^{=}$ in ammoniated waters is from the latter reaction. Let X be the amount of $CaCO_3$ formed, then equation [9] is transformed to

$$K_{CaCO_3} = [Ca^{++} - X]\,[CO_3^{=} - X] \qquad [15]$$

and X may be computed from

$$X = \frac{[Ca^{++} + CO_3^{=}] - \{[Ca^{++} + CO_3^{=}]^2 - 4([Ca^{++}]\,[CO_3^{=}] - K_{CaCO_3})\}^{1/2}}{2} \qquad [16]$$

The overall reaction for lime precipitation depends upon whether the system is open (equation [17]) or closed (equation [18]). In the first case, 2 moles of HCO_3^{-} are required for each mole of $CaCO_3$ formed. For each mole of $CaCO_3$ formed, 1 mole of CO_2 gas is lost in the open system. Conversely, CO_2 is not released in a closed system, and only 1 mole of HCO_3^{-} is required for each mole of $CaCO_3$ formed. For purposes of this investigation, and in pipelines, much of the precipitation takes place in a closed system, and only at cracks, standpipes, control boxes, and other sites in contact with the atmosphere will open-system conditions prevail.

$$Ca^{++} + 2HCO_3^{-} \rightleftarrows CaCO_3\downarrow + CO_2\uparrow + H_2O \qquad [17]$$

$$Ca^{++} + HCO_3^{-} \rightleftarrows CaCO_3\downarrow + H^{+} \qquad [18]$$

The preceding discussion is but one of many theoretical approaches to the problem (for example, Frear and Johnston, 1929; Langelier, 1936; Moore, 1939; Larson and Buswell, 1942; Dye, 1958; Garrels, 1960; Akin and Lagerwerff, 1965*a*), and additional considerations are required for successful prediction of lime precipitation. These include the inhibiting effect of Mg on lime precipitation, and formulations describing the stability or instability of waters with respect to lime.

CRYSTALLIZATION

Supersolubility, Nucleation, and Crystal Growth

Crystallization is a dynamic process. When solutions of two ions which may form a precipitate are brought together, the solubility-product constant of the salt for these ions may be exceeded, and the solution then becomes supersaturated. After a time (which may vary from a fraction of a second to hours or even years), crystallization begins with the formation of colloidal-sized particles, called nuclei or crystal seeds. During and after nucleation a different process takes over, in which the nuclei grow by coagulation of the colloidal particles or by incorporation of ions from the solution phase into the solid phase. The solid (precipitant) formed may be crystalline, with a definite lattice system, or it may be noncrystalline (amorphous).

A schematic concept of supersolubility is shown in Appendix figure 2. The solubility of a salt depends upon its concentration, other solutes present in the ambient solution, and temperature.

Nucleation takes place only in a supersaturated solution. The probability of its occurrence increases with the degree of supersaturation expressed by the ratio (Salutsky, 1959),

$$\text{Supersaturation ratio (S.R.)} = (K_{ss}/K_{sp})^{1/2} \qquad [19]$$

where K_{ss} and K_{sp} are the ion-activity products in the supersaturated and saturated states, respectively. When S.R. is very small, only a few nuclei are formed, and precipitation may take place for several days or months. As this ratio increases, the stability of the solution decreases and nucleation readily occurs. The nucleation process governs the nature and purity of the resulting precipitate. When many nuclei are formed, precipitation will be rapid, crystals small in size, and purity low. Conversely, if only a few nuclei are formed, precipitation will be slower, with larger crystals, and of higher purity.

Many theories on the mechanisms of crystal growth have been proposed (see, for example, Buckley, 1951); it suffices to state that crystal growth continues until supersaturation of the precipitating materials is eliminated. In general, larger crystals grow at the expense of smaller ones, because smaller crystals are more soluble. If, upon nucleation, coagulation and coalescing of colloidal particles (aggregation velocity) predominate over orderly crystalline growth (orientation velocity), the precipitate formed is often either gelatinous or in a suspended state, and would therefore be unsuitable for sealing leaks. Thus, crystallization rate is an important factor.

Coprecipitation of Impurities and Magnesium

Colloidal-sized impurities present in solutions often act as seeds for crystallization, and these foreign particles may be mechanically occluded or trapped by the crystal layers. A significant effect is the tendency for suspended impurities (such as silt, clay, dispersed organic matter, and algae) to trigger spontaneous precipitation of lime. Such precipitants are unsuitable for sealing action because they remain in suspension or are softly consolidated and porous.

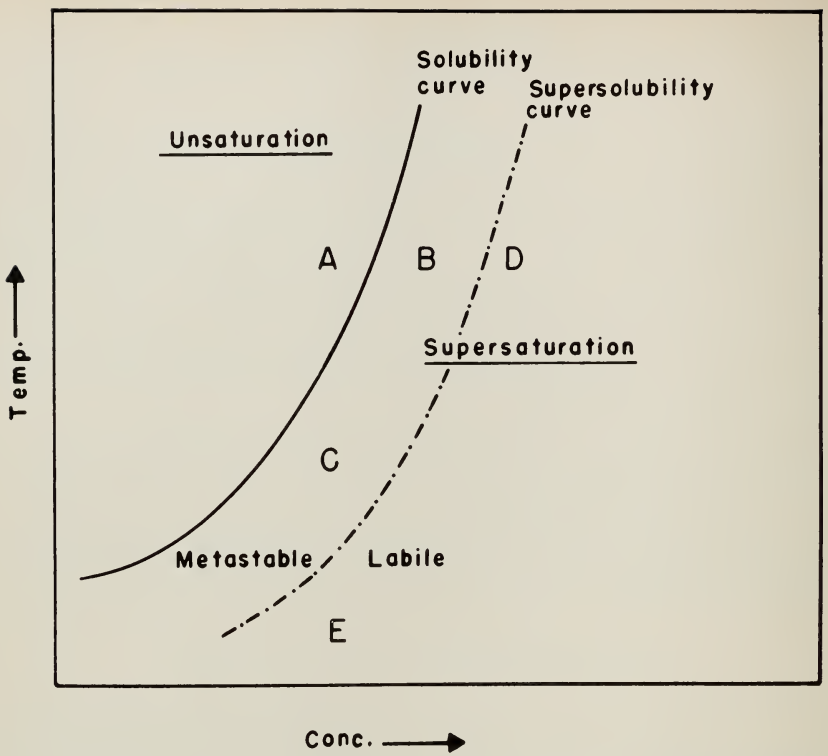


Fig. 2A. Schematic diagram of solubility-supersolubility curves and regions. (Modified from Van Hook, 1961.) If concentration products (activity products) of two ions of the salt in solution are less than the solubility-product constant (activity-product constant), the solution is said to be undersaturated, and occupies a point somewhere to the left of the solubility curve, A. If solute concentrations are increased to B, or if temperature is reduced to C, solution is said to be saturated. Crystallization does not occur spontaneously in the metastable zone bounded by solubility and supersolubility curves. If concentration is further increased to D (supersaturated), however, or temperature is further reduced to E (supercooled), a condition of supersolubility exists. Labile zone, where spontaneous generation of nuclei takes place, is beyond limits of the supersolubility curve. Nucleation and crystal growth continue until chemical equilibrium is established between the salt and its solution.

Coprecipitation may also occur by adsorption on electrostatically charged surfaces of crystals that attract ions of opposite charge. According to Berner (1966), $CaCO_3$ has an exchange capacity ranging from 6 to 12 m.e. per 100 gm. Adsorption of Mg^{++} by $CaCO_3$ has been reported by Brooks, Clark, and Thurston (1950) and Berner (1966). These investigators also discuss the substitution of smaller Mg^{++} for Ca^{++} in the crystal lattice of $CaCO_3$. Because of coprecipitation and impurities, the $CaCO_3$ precipitants observed under a microscope were not always ideal crystals, but showed various degrees of deformity. There is also evidence that Mg^{++} inhibits crystallization of $CaCO_3$ (Brooks, Clark, and Turner, 1950; Berner, 1966; Akin and Lagerwerff, 1966*b*), apparently by formation of nucleation-inhibiting or surface-protective layers of adsorbed Mg^{++}.

In magnesium-rich waters, $Mg(OH)_2$ is preferentially formed at higher pH,

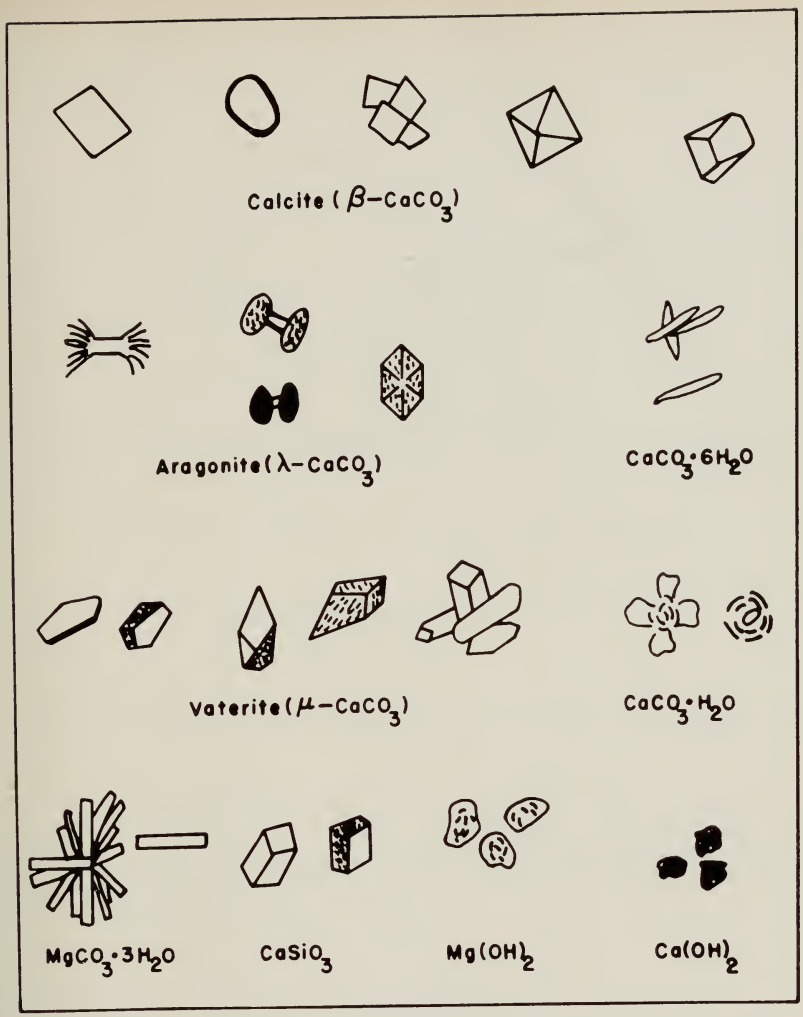


Fig. 3A. The several forms of calcium carbonate and other Ca and Mg salts.

and $MgCO_3 \cdot 3H_2O$ at lower pH, when Ca^{++} is low or depleted through precipitation (Kline, 1929).

Crystalline Forms of Lime and Solubility-product Constants

Calcite, aragonite, and vaterite are found in nature as polymorphs; that is, they have the same chemical composition ($CaCO_3$), but different crystalline forms (Hurlbutt, 1955). Calcite usually occurs as rhombohedrals and octahedrals while aragonite occurs in a variety of hexagonal forms frequently twinned (paired or coupled) or dumbbell-shaped. Vaterite has been reported as a distinct form of anhydrous calcium carbonate (Brooks, Clark, and Turner, 1950). Sketches of these and other crystals are shown in Appendix figure 3.

The hydrated forms of calcium carbonate are monohydrate ($CaCO_3 \cdot H_2O$) and hexahydrate ($CaCO_3 \cdot 6H_2O$). Monohydrates are identified as spherulitic grains;

hexahydrates have been observed as birefringent needles. Photomicrographs of all of these forms, except vaterite, are to be found in the literature (Brooks, Clark, and Turner, 1950; Buehrer and Reitemeir, 1940). The trihydrate and pentahydrate forms and amorphous hydrated calcium carbonate have been reported, but little is known about them (Johnston *et al.*, 1916).

Calcite is the most stable form of lime. Aragonite and vaterite are said to be less stable, but the difference between these two is relatively small. The monohydrate and hexahydrate are metastable forms which may exist for long periods before decomposing into calcite and aragonite upon dehydration. All of these forms were precipitated in the laboratory from salt solutions and natural waters, and have exhibited strong adherence to laboratory glassware.

The crystalline forms of $CaCO_3$ have different solubilities, which make quantitative predictions on lime precipitation quite formidable. The solubility-product constants (K_{sp}) of calcite and aragonite are 4.8×10^{-9} and 6.0×10^{-9}, respectively (Sillen, 1964). The K_{sp} values for other forms are not known, but it has been estimated that the solubility of vaterite is 20 ppm and of calcium carbonate monohydrate and hexahydrate about 30–40 ppm (Brooks, Clark, and Turner, 1950).

APPENDIX B: PREDICTIONS ON LIME PRECIPITATION

The chemistry of lime has received considerable attention from many fields of interest, particularly the waterworks industry, geochemistry, and agriculture. Contributions from these fields include indices or parameters for indicating the stability or instability of waters with respect to lime. In quantitative treatments, attempts are made to predict the solubility of lime. It would be desirable to have a method for predicting qualitatively, if not quantitatively, precipitation of lime in waters treated with ammonia and other additives. If such predictions are not possible, waters will have to be tested individually by trial and error, a method requiring considerable time and expense. From certain formulations presented in the literature, and with appropriate modifications thereof, we attempt in this section to predict lime precipitation by using the data from the table in Appendix C.

Mg Precipitation

The solubility of $Mg(OH)_2$ is defined by

$$K_{Mg(OH)_2} = [Mg^{++}][OH^-]^2 \qquad [20]$$

The OH^- concentration can be estimated from NH_3 concentration and equation [3]. Letting X be the amount of $Mg(OH)_2$, equation [20] is extended to

$$K_{Mg(OH)_2} = [Mg^{++} - X][OH^- - X]^2 \qquad [21]$$

which leads to

$$X^3 - ([Mg^{++}] + 2[OH^-])X^2 + ([Mg^{++}][OH^-] + [OH^-]^2)X - ([Mg^{++}][OH^-]^2 - K_{Mg(OH)_2}) = 0 \quad [22]$$

The amount of $Mg(OH)_2$, X, can be calculated from equation [22] by successive approximations. Apparently a substantial portion of the Mg^{++} coprecipitated as $Mg(OH)_2$ in these waters because of a fair agreement between experimental Mg^{++} precipitation and the calculated $Mg(OH)_2$ (table 10). It should be noted, however, that similar amounts of $Mg(OH)_2$ were calculated for waters that had high Mg^{++} contents but were not listed in table 10 because Mg^{++} coprecipitated only in trace amounts. Thus it is apparent that the chemical and physical factors affecting Mg^{++} precipitation are still obscure and are not necessarily related to inhibiting effects of Mg on lime precipitation.

Supersaturation Ratio, Driving-force Index

The supersaturation ratio, defined by equation [19], is a measure of the saturation status of a solution; with increasing ratio, the lime crystallizes more readily, and presumably more precipitation of lime occurs. K_{sp} in this equation is the activity-product constant for calcite, having a value of 4.82×10^{-9} at 25° C, and K_{ss} is the product of the activities of Ca^{++} and $CO_3^{=}$ in the water or solution.

$$K_{ss} = a_{Ca}\, a_{CO_3} = (Ca^{++})\, \gamma_{Ca}\, (CO_3^{=})\, \gamma_{CO_3} \quad [23]$$

The activity of an ion, a, is the product of its molar concentration, denoted by parentheses, and activity coefficient, γ. The ionic activity coefficient may be obtained from the Debye-Huckel equation,

$$\log \gamma_i = \frac{-0.509\, Z_i^2\, \mu^{1/2}}{1 + 0.328\, A\mu^{1/2}} \quad [24]$$

where Z_i is the charge of ion species, i, A is the effective size of the hydrated ion, and μ is the ionic strength. Values of A for Ca^{++} and $CO_3^{=}$ are reported (Kielland, 1937) to be 6 and 4.5 $A°$ respectively. The ionic strength, in turn, is obtained from

$$\mu = \tfrac{1}{2} \sum_{i=1}^{n} C_i\, Z_i^2 \quad [25]$$

where C_i is the molar concentration of ion species, i. It is also of interest to note that Bower *et al.* (1965) obtained a regression equation for ionic strength from 200 natural surface and ground waters ranging in total cation concentration from 1 to 50 m.e. per liter,

$$1000\, \mu = 1.3477\, C + 0.5355 \quad [26]$$

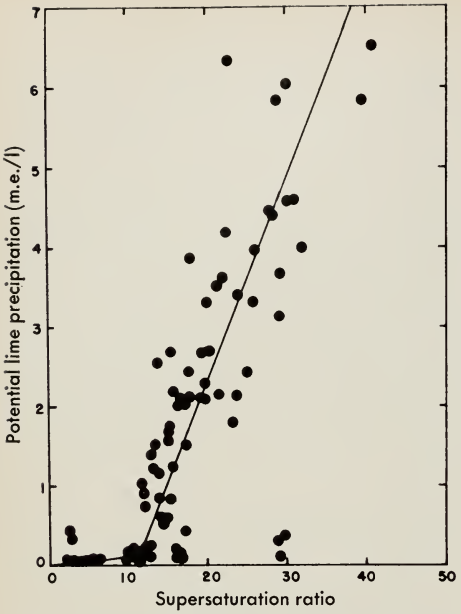


Fig. 4A. Supersaturation ratio of 100-ppm NH_3 waters (see Appendix C) and potential lime precipitation, defined as the product of experimentally determined $CaCO_3$ precipitation and reciprocal of the Mg inhibiting factor.

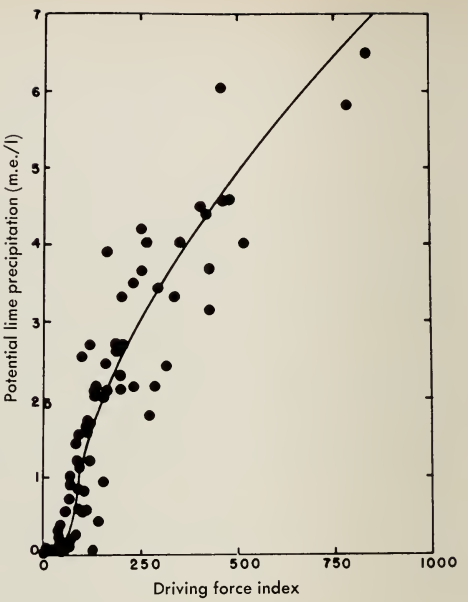


Fig. 5A. Driving-force index of 100-ppm NH_3 waters and potential lime precipitation values.

where C is the total cation concentration in m.e. per liter. When water analyses are incomplete, C may be estimated from electrical conductivity. Additionally, Hem (1961) presented a graphic aid in computing activity coefficients as related to ionic strength.

The concentrations of Ca^{++} and HCO_3^- are obtained from chemical analysis of the water and any additional amendments of Ca^{++} and/or HCO_3^-. With ammoniation, part of the HCO_3^- is converted to $CO_3^=$ and the concentration may be calculated from equation [14].

The supersaturation ratio of waters (listed in Appendix C) was calculated by the above method for the 100-ppm NH_3 treatments. A plot of this index and experimentally determined lime precipitation resulted in a scatter diagram. The supersaturation ratio and other indices do not take into account the inhibiting effect of Mg on lime precipitation. One method for including the Mg factor is to take the product of experimental lime precipitation and the reciprocal of the Mg inhibiting factor (figure 11). The new value so obtained may be considered to represent the potential precipitation of lime, i.e., precipitation in the absence of Mg^{++} in the water. When the calculated potential lime precipitation values are plotted against the supersaturation ratio (Appendix fig. 4), a definite trend is realized, although scattering of points is still evident. A somewhat linear relationship is apparent wherein lime begins to form when the supersaturation ratio is about 11.

McCauley (1960) has proposed another index, termed the driving-force index,

which is defined as

$$DFI = \frac{Ca^{++} \times CO_3^{=}}{K_s' \times 10^{10}} \quad [27]$$

where Ca^{++} and $CO_3^{=}$ are in terms of ppm $CaCO_3$, and K_s', the solubility product constant of calcite corrected for dissolved solids and temperature, is also in ppm. A driving-force index of 1.0 represents a water that is stable insofar as lime is concerned. McCauley suggests that $CO_3^{=}$ concentration be obtained from a nomogram (for example, fig. 11 in Orland, 1965), and K_s' be estimated from another nomogram (for example, fig. 7 in Dye, 1958). But in our study, $CO_3^{=}$ is formed primarily from ammoniation (equation [11]), and little from the dissociation of HCO_3^{-} (equation [6]). Therefore $CO_3^{=}$ estimated from equation [14] was used instead. Since the scale on the nomogram for K_s' was found to be inaccurate, K_s' was computed from K_{sp}/γ^2.

A curvilinear relation between the driving-force index of waters treated with 100 ppm NH_3 and potential lime precipitation calculated from experimental data is shown (Appendix fig. 5).

Saturation Index, Stability Index, pH_s

Another widely used index in the water treatment industry is Langelier's (1936) saturation index defined by

$$SI = pH_a - pH_s \quad [28]$$

where pH_a is the actual pH of the water and pH_s is the pH of the water when in equilibrium with solid $CaCO_3$. If SI is positive, lime precipitates, and if SI is negative, the water will dissolve lime. The pH_s is calculated from the following expression

$$pH_s = pK_2' - pK_s' + p\text{Ca} + p\text{Alk.} + \log\left[1 + \frac{2K_2'}{H^+}\right] \quad [29]$$

where $pK_2' - pK_s'$ are the negative logarithms of the second dissociation constant for carbonic acid and the solubility product constant of calcite, respectively, both corrected for ionic strength; pCa and pAlk. are the negative logarithms of the molar concentration of Ca^{++} and the equivalent concentration of titratable base; and the last term is a correction factor to be used when pH_s exceeds 9. Tabulated values for $pK_2' - pK_s'$ and the last term in equation [29] are found in Langelier (1936).

The saturation index describes the calcium carbonate saturation condition of a water under closed-system conditions, but does not take into account changes in water composition—for example, when the water is ammoniated. Nevertheless, because this index is widely used, we explored the application of it, or its parameters, to this study. The relation between the saturation index of waters listed in Appendix C and their potential lime precipitation values is given in Appendix figure 6. A curvilinear trend is obtained which is similar to published data (Langelier, 1936; Ryznar, 1944). Because small changes in the vicinity of a

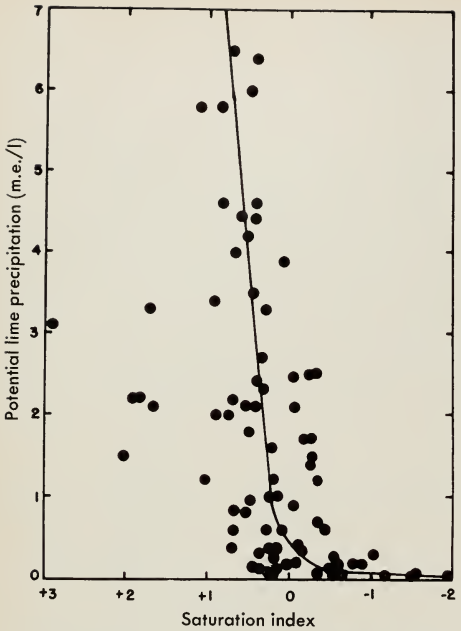


Fig. 6A. Saturation index of waters, before ammoniation, and potential lime precipitation values calculated from 100-ppm NH_3 waters.

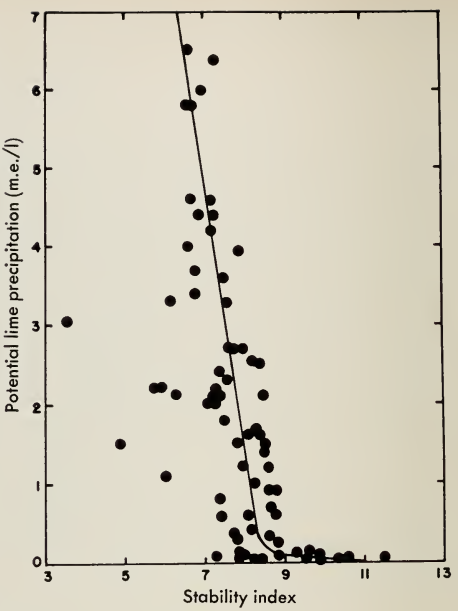


Fig. 7A. Stability index of waters, before ammoniation, and potential lime precipitation values calculated from 100-ppm NH_3 waters.

saturation index of 0.0 $\pm$ 0.5 are related to large differences in potential lime precipitation, the index appeared to be unsuitable for our study.

The stability index for waters, proposed by Ryznar (1944), is an empirical modification of the saturation index. According to Langelier (1936), the saturation index provides a means of ascertaining the directional tendency of the water to deposit lime, and is in no way a measure of its capacity. Ryznar (1944) points out that in some cases two waters may have an identical saturation index but widely different scale-forming tendencies. To overcome this anomaly, Ryznar suggests placing emphasis on pH_s by,

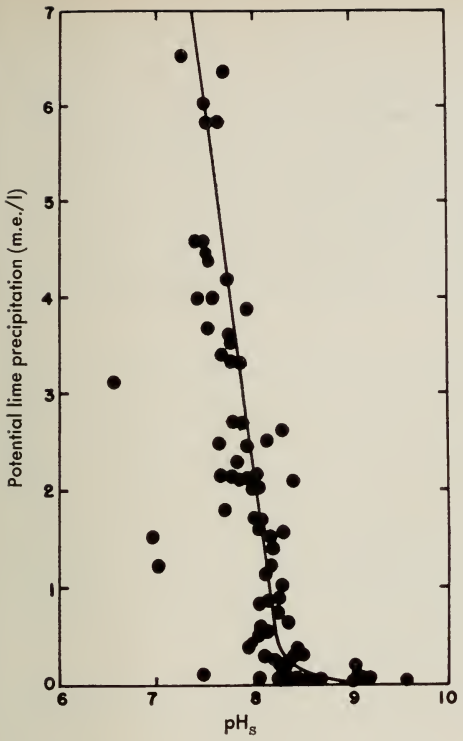
$$\text{Stability index} = 2pH_s - pH_a \qquad [30]$$

A plot of potential lime precipitation values calculated from data obtained from waters treated with 100 ppm NH_3 and the stability index is presented in Appendix figure 7. A marked improvement over the saturation index is noted in curvilinear relations. Lime appears to form when the stability index is less than 9.

In a more recent study by Bower *et al.* (1965), pH_s of synthetic waters was highly correlated with the solubility of lime. Substantial correlation between pH_s of waters before ammoniation, and potential lime precipitation values is evident (Appendix fig. 8).

Momentary Excess, Quantitative Prediction

A more quantitative measure of a water's degree of saturation with respect to



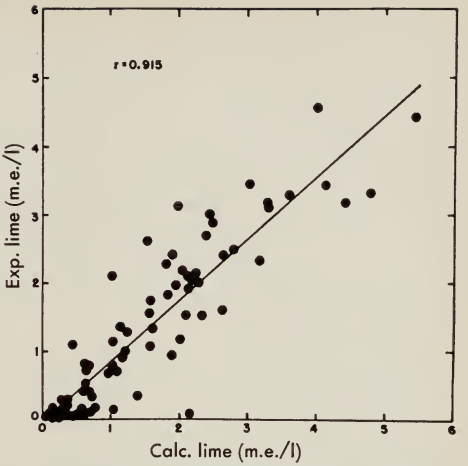


Fig. 9A. Above: Prediction of experimentally determined $CaCO_3$ precipitation in 100-ppm NH_3 waters from equation [32] and Mg inhibiting factor (MIF).

Fig. 8A. Left: Relation between pH_s of waters, before ammoniation, and potential lime precipitation values obtained from 100-ppm NH_3 waters.

lime was suggested by Dye (1958). The momentary excess or initial precipitation of lime is calculated by the following expression

$$(Ca^{++} - X)\ (CO_3^{=} - X) = K_s' \times 10^{10} \qquad [31]$$

where X is the momentary excess, and the parentheses denote concentration in terms of ppm $CaCO_3$. In a similar manner, Tanji and Doneen (1966*a*) computed lime precipitation by

$$(Ca^{++} - X)\ \gamma_{Ca}\ (CO_3^{=} - X)\ \gamma_{CO_3} = K_{sp} \qquad [32]$$

where parentheses denote molar concentration and γ is the ionic activity coefficient.

Since equation [32] is more precise than equation [31], it was applied to the waters in this study. Equation [32] was solved for X after $CO_3^{=}$ was obtained from equation [14]. The predicted lime precipitation, X, was found to be much higher than the experimental values. This discrepancy was reduced when X was multiplied by the respective Mg inhibiting factor of the water. Substantial overall agreement between experimental and calculated values, $r = 0.915$, is indicated in Appendix figure 9.

Discussion on Predictions

Several methods for prediction of lime precipitation in ammoniated waters

have given varied results. These computations indicate that precise predictions are not readily obtainable.

With some exceptions, the precipitation of lime from waters was carried out at room temperatures of 22 ± 2° C. The constants appearing in the equations were values applicable to 25° C. Moreover, the K_{sp} values employed were for calcite. In the experimental waters of widely differing chemical composition, crystalline species other than calcite precipitated with solubilities greater than calcite. This may be the reason that the regression line in Appendix figure 9 is less than a 1:1 correspondence. Furthermore, some of these calculations assumed chemical equilibrium, which may or may not have been attained over the 48-hour precipitation period.

The inhibiting effect of Mg on lime precipitation is not accounted for in any of the published formulas. Adjustments were made by calculating the potential precipitation of lime from these waters by taking the product of experimental lime data and its reciprocal Mg inhibiting factor. The various qualitative indices were then evaluated against potential lime values. For the quantitative method (equation [32]), the first approximation on lime precipitation, X, was modified by the Mg factor to obtain predicted values. The Mg factor was empirically derived from limited data, but its application to experimental waters appears to be significant. The probability of overcorrection or undercorrection for Mg^{++} effects in certain waters, however, should not be discounted.

For more quantitative consideration, other factors should be accounted for, such as: the formation of $Mg(OH)_2$; ion pairs of $CaSO_4$ (Tanji and Doneen, 1966*b*); $MgCO_3$ and $CaCO_3$ (Garrels, Thompson, and Siever, 1961); and complexes of $Ca(HCO_3)^+$, $Mg(HCO_3)^+$, and $(MgOH)^+$ (Garrels *et al.*, 1961). These computations can, however, become quite unmanageable or lengthy.

An examination of widely divergent points, in Appendix figures 4 through 9, indicates that some waters recur frequently, but many do not. The reasons for their deviation from the trend are not very apparent.

Because of the complexity and dynamic nature of lime chemistry in ammoniated waters, the qualitative methods of predicting lime precipitation are less than satisfactory. The slopes obtained from the relations between potential lime precipitation and various qualitative indices are so steep that small changes of the index result in large changes in predictions. The quantitative method presented above, however, not only yields a more accurate prediction but also predicts in terms of actual lime instead of potential lime precipitation.

APPENDIX C

POTENTIAL FOR LIME PRECIPITATION OF NATURAL AND RECONSTITUTED AMMONIATED WATERS IN CALIFORNIA

(NOTE: Figures are averages of duplicate determinations. Ca^{++} concentrations are in ascending order as are HCO_3^- concentrations within a Ca^{++} concentration range. Mg^{++} concentrations are also arranged in increasing order for waters with similar Ca^{++} and HCO_3^- contents. Experimental values for precipitation and pH are not necessarily equilibrium values because these were not the objective of the test. Previous studies indicated, however, that the 48-hour test approached equilibrium.)

Water no.	Water composition							Water treated with NH_3 at:					
								50 ppm		100 ppm		150 ppm	
	Ca^{++}	HCO_3^-	Mg^{++}	Na^+	$SO_4^=$	Cl^-	pH	$CaCO_3$ precip.	pH after precip.	$CaCO_3$ precip.	pH after precip.	$CaCO_3$ precip.	pH after precip.
	m.e./l	*m.e./l*	*m.e./l*	*m.e./l*	*m.e./l*	*m.e./l*		*m.e./l*		*m.e./l*		*m.e./l*	
1	0.21	0.37	0.08	0.08	0.06	0.05	7.60	0.03	10.15	0.04	10.42	0.04	10.59
2	0.22	1.16	0.27	0.90	0.13	0.13	8.74	0.04	10.10	0.04	10.32	0.04	10.51
3	0.21	1.14	0.29	0.89	0.13	0.19	8.61	0.02	10.24	0.02	10.42	0.02	10.56
4	0.20	1.13	0.31	0.89	0.13	0.15	8.53	0.01	10.29	0.02	10.54	0.02	10.64
5	0.42	0.56	0.18	0.15	0.10	0.13	7.51	0.05	10.29	0.05	10.46	0.05	10.68
6	0.41	0.59	0.45	0.15	0.10	0.36	8.56	0.03	10.17	0.04	10.38	0.05	10.56
7	0.43	0.61	0.98	0.15	0.10	0.81	8.28	0.03	10.32	0.06	10.55	0.06	10.68
8	0.45	2.12	0.22	2.00	0.17	0.24	8.61	0.24	9.85	0.28	10.02	0.32	10.16
9	0.41	2.13	0.58	1.60	0.31	0.31	8.69	0.02	9.96	0.03	10.18	0.04	10.32
10	0.39	2.11	0.60	1.58	0.29	0.34	8.72	0.01	10.05	0.01	10.26	0.02	10.39
11	0.56	2.10	1.30	0.64	0.17	0.16	8.39	0.05	10.15	0.06	10.36	0.07	10.46
12	0.52	2.87	0.85	2.01	0.40	0.42	8.72	0.04	9.96	0.06	10.22	0.08	10.41
13	0.53	2.81	1.24	2.01	0.42	0.84	8.72	0.02	10.13	0.04	10.35	0.05	10.44
14	0.74	0.61	0.57	1.85	2.39	0.42	7.34	<0.01	9.88	0.02	10.08	0.03	10.19
15	0.95	0.74	0.75	2.36	3.33	0.54	7.51	<0.01	9.92	0.02	10.18	0.02	10.31
16	0.76	1.07	0.37	0.30	0.25	0.32	7.46	0.05	10.02	0.15	10.31	0.20	10.42
17	0.85	1.09	1.32	0.30	0.23	1.20	7.65	0.01	10.18	0.05	10.30	0.11	10.55
18	0.88	2.63	2.03	0.40	0.29	0.24	8.47	0.03	9.83	0.09	9.97	0.31	10.11
19	0.87	4.14	0.42	3.20	0.40	0.29	8.99	0.72	10.18	0.76	10.42	0.77	10.56
20	0.86	4.35	1.29	3.49	0.85	0.65	7.88	0.07	9.89	0.20	10.08	0.21	10.29
21	1.08	1.79	0.74	2.43	3.38	0.48	8.18	0.13	10.00	0.15	10.14	0.18	10.24
22	1.00	2.20	0.66	1.79	0.31	0.83	8.21	0.32	9.90	0.41	10.08	0.48	10.30
23	1.12	2.15	1.26	0.62	0.14	0.66	8.35	0.16	10.10	0.32	10.30	0.41	10.38
24	0.94	2.19	3.70	1.65	0.27	4.16	7.91	0.04	9.79	0.11	10.02	0.12	10.34
25	0.97	2.78	0.74	4.20	3.33	0.51	8.32	0.68	9.70	0.79	9.90	0.80	10.02
26	0.98	2.78	0.85	1.99	0.42	0.90	8.72	0.45	10.04	0.54	10.24	0.56	10.51
27	1.08	2.73	2.45	2.01	0.42	2.63	8.77	0.15	10.30	0.18	10.52	0.21	10.63
28	0.90	3.07	3.07	0.53	0.19	2.58	7.93	0.07	9.76	0.12	9.84	0.13	10.21
29	0.99	3.81	0.71	5.44	3.64	0.59	8.05	0.81	9.64	0.87	9.88	0.90	10.01
30	1.26	1.22	0.32	0.94	0.17	1.17	8.21	0.51	10.10	0.78	10.40	0.81	10.54
31	1.34	2.31	0.51	8.25	5.10	3.26	7.66	0.64	9.77	0.71	10.12	0.84	10.33
32	1.50	1.05	1.08	7.60	8.32	1.71	7.75	0.06	9.69	0.13	10.06	0.37	10.28
33	1.80	1.03	0.36	0.31	0.23	1.19	7.85	0.84	10.10	1.09	10.34	1.26	10.53
34	1.88	2.05	2.21	0.66	0.14	2.67	8.86	0.94	9.81	1.13	10.10	1.17	10.34

35	1.37	2.04	4.15	0.67	3.14	4.79	8.77	0.34	10.01	0.67	10.24	0.78	10.42
36	1.76	4.19	1.31	3.45	0.79	1.64	8.19	1.16	9.82	1.28	10.12	1.33	10.22
37	1.92	7.98	5.41	2.48	1.04	0.72	7.89	0.80	9.48	1.10	9.84	1.10	10.10
38	2.09	0.49	0.07	0.19	1.25	0.91	8.33	0.28	10.30	0.34	10.52	0.47	10.63
39	2.24	0.71	0.20	0.27	2.16	0.14	8.43	0.80	10.04	0.96	10.24	1.12	10.51
40	2.23	1.20	0.31	0.91	0.17	2.16	8.24	1.22	9.96	1.54	10.30	1.57	10.40
41	2.09	1.18	1.04	0.96	1.77	0.96	7.86	1.10	9.94	1.26	10.23	1.32	10.50
42	2.09	1.18	2.21	0.93	1.77	2.16	7.88	0.77	9.96	0.88	10.25	0.96	10.50
43	2.08	1.14	3.14	0.92	1.77	3.12	7.94	0.60	10.16	0.68	10.37	0.74	10.52
44	2.07	1.13	4.16	0.82	0.19	6.22	7.66	0.06	10.09	0.09	10.28	0.10	10.45
45	2.16	1.13	6.60	0.82	0.19	8.77	7.78	<0.01	10.02	0.02	10.15	0.06	10.39
46	2.20	1.41	0.12	1.06	1.97	0.14	8.26	0.04	9.83	0.06	9.98	0.08	10.05
47	2.11	2.11	1.23	0.66	0.14	1.67	8.30	1.40	9.78	1.57	9.97	1.60	10.30
48	2.15	1.87	8.31	0.53	0.19	7.74	7.89	0.23	9.70	0.25	9.97	0.30	10.18
49	2.11	3.21	0.67	8.75	6.24	3.20	8.39	1.70	10.07	1.82	10.39	1.85	10.54
50	2.09	4.10	2.58	1.33	0.40	1.34	8.03	1.32	9.92	1.36	10.20	1.41	10.34
51	2.40	1.64	0.22	1.14	2.08	0.19	9.61	1.85	9.66	2.01	9.89	2.98	10.09
52	2.28	2.20	0.62	1.60	2.19	0.35	8.15	1.86	9.61	1.97	10.01	2.01	10.25
53	2.36	2.12	3.91	1.65	2.29	3.60	7.99	1.34	9.53	1.75	9.79	1.86	9.95
54	2.28	2.54	0.22	2.14	2.08	0.19	9.67	1.97	9.58	2.05	9.96	2.09	10.16
55	2.29	3.28	0.20	3.20	2.08	0.19	9.57	2.10	9.57	2.15	9.92	2.18	10.10
56	2.71	1.12	1.74	0.32	0.23	3.68	8.53	0.81	9.87	1.17	10.31	1.44	10.40
57	2.61	1.12	3.97	0.31	0.23	6.00	8.36	0.85	10.14	1.00	10.39	1.27	10.56
58	2.47	2.75	1.24	2.07	2.39	1.06	8.26	1.99	9.41	2.09	9.68	2.17	9.89
59	2.62	4.41	2.10	3.56	0.71	2.63	7.96	2.10	9.41	2.19	9.75	2.21	9.94
60	2.79	1.07	0.35	0.30	0.23	2.20	7.75	1.45	9.81	1.63	10.20	1.70	10.35
61	2.97	2.26	0.60	8.25	7.59	3.11	8.06	2.13	9.71	2.41	10.08	2.48	10.29
62	2.99	2.03	2.18	7.60	8.32	1.71	7.75	1.52	9.69	1.92	10.06	2.05	10.28
63	2.79	3.04	2.31	8.25	8.32	1.71	8.23	2.02	9.78	2.43	10.08	2.46	10.28
64	2.94	4.11	2.82	1.30	0.40	2.38	8.21	2.19	9.44	2.28	9.84	2.36	10.04
65	2.80	4.00	5.48	1.20	2.08	3.40	8.73	1.88	9.84	2.10	10.10	2.30	10.25
66	3.43	2.79	0.38	2.14	3.54	0.28	9.48	3.00	9.56	3.16	10.11	3.20	10.30
67	3.34	3.71	0.20	3.50	3.53	0.30	9.42	3.03	9.59	3.13	9.97	3.15	10.15
68	3.18	4.57	4.84	1.52	1.08	0.72	7.95	2.29	9.02	2.90	9.41	2.96	9.62
69	3.44	4.28	5.50	2.92	2.25	5.22	8.37	2.31	9.78	3.63	10.12	2.93	10.34
70	3.20	5 60	2.06	....	1.04	1.36	7.11	2.38	9.24	2.70	9.70	2.75	9.96
71	3.70	1.14	0.36	0.30	3.16	0.19	7.60	1.74	9.91	2.34	10.26	2.35	10.56
72	3.61	1.11	2.65	0.32	2.71	2.98	8.73	1.27	9.87	1.54	10.20	1.55	10.50
73	3.59	1.10	5.17	0.32	2.81	5.60	8.65	1.15	10.19	1.34	10.35	1.44	10.56
74	3.82	2.11	0.39	1.25	3.44	0.29	8.62	3.01	9.82	3.27	10.20	3.34	10.42
75	3.76	1.98	2.35	7.08	9.36	1.69	8.12	2.15	9.52	2.49	9.92	2.61	10.14
76	3.75	4.17	1.26	3.53	3.33	0.64	8.11	3.18	9.36	3.45	9.80	3.46	9.94
77	3.68	4.12	3.33	3.05	2.81	3.16	8.31	2.71	9.65	3.01	10.13	3.12	10.30
78	3.76	7.84	5.55	2.53	2.89	0.72	7.95	2.93	9.26	3.13	9.64	3.29	9.90
79	4.30	2.13	0.64	7.92	7.81	3.13	7.96	3.06	9.12	3.46	9.55	3.58	9.79
80	5.04	5.54	2.36	....	2.91	1.34	8.37	3.72	8.70	4.56	9.58	4.57	9.86
81	5.65	1.97	2.74	7.20	12.49	1.58	8.10	2.91	9.29	3.18	9.71	3.31	9.94
82	7.43	2.23	0.52	8.04	10.93	3.05	8.12	4.08	9.07	4.45	9.51	4.53	9.83
83	8.34	1.92	2.93	7.20	15.61	1.58	8.12	3.06	9.28	3.33	9.74	3.37	9.96

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